NANOSTRUCTURED HOLLOW INORGANIC MATERIALS

Prasanga Gayanath Mantilaka
Board of Study in Chemical Sciences

Inorganic materials containing porous structures (Holes) are known as inorganic hollow materials (Liu *et al.*, 2014). Most of these materials are prepared by fabrication of nanoparticles. Some examples for inorganic materials are calcium carbonate, titanium dioxide, carbon, silica, calcium phosphates/hydroxyapatite and their composites (Zhao and Wang, 2012). Hollow structures of these inorganic materials have potential applications in catalysis, sensors, lightweight fillers, confined-space chemical reactors, low-dielectric-constant thin films, photonic crystals, controlled drug delivery, biomedical diagnosis and therapy, anode materials in lithium ion batteries and so on (Hou *et al.*, 2010). Therefore, nanostructured hollow materials have gained a great attraction in recent years. One hollow inorganic material which can be used for numerous applications by filling its hole by various other materials depending on end use. For example, calcium carbonate hollow spheres are filled by various drugs in order to use as drug delivery systems. Herein, drug is encapsulated by calcium carbonate and hence, the drug is only released at the target infected cells. Another recent study reports that the carbon (graphite) nanocapsules can be used as an electrode material for hydrogen peroxide detection (Liu *et al.*, 2014). Herein, electrically conductive graphite capsule is filled by enzymes in order to use as a detector (Liu *et al.*, 2014). Hollow materials are mainly characterized with the help of Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). SEM and TEM images of few hollow inorganic materials are shown in Figure 01.

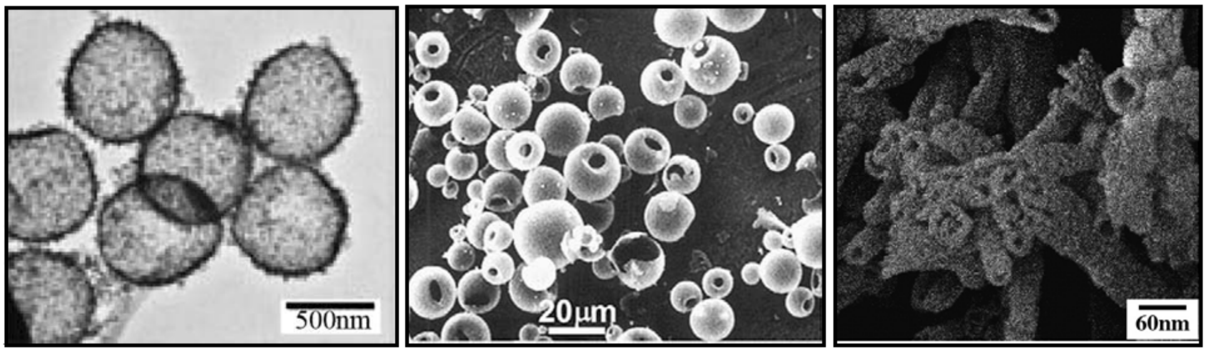

Figure 01: Electron Microscopic images of inorganic hollow materials in literature

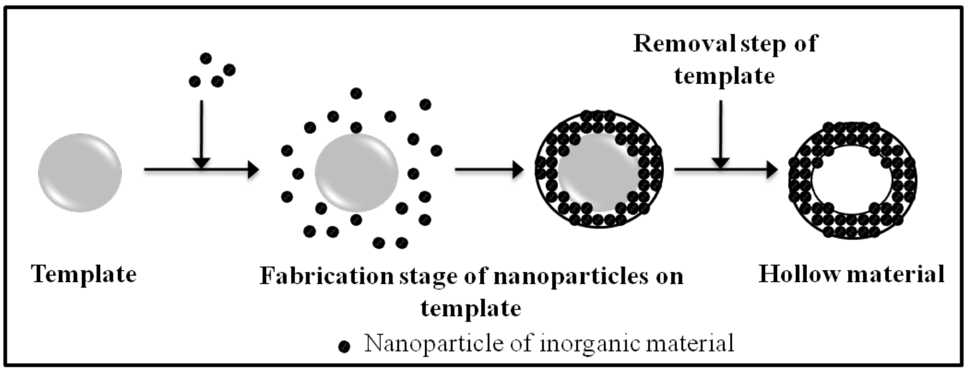

Figure 02: Formation mechanism of nanostructured hollow materials

Hole of the particle is produced using templates. Nanoparticles of the inorganic materials are fabricated on the template and later, after the fabrication, the template is removed from the system to form the hole. The formation mechanism is schematically represented in Figure 02. There are two types of templates as soft template and hard template (Hou *et al.*, 2010). Soft templates are in liquid or gas phase while the hard template is a solid material (Mantilaka *et al.*, 2014; Hou *et al.*, 2010). For example, silica nanoparticles are fabricated on calcium carbonate template and later, calcium carbonate template is removed from the system by treating the final product with an acid in order to produce hollow silica (Zhao *et al.*, 2008). Herein, silica is acid resistant while the calcium carbonate is digested in acid. Polymer/surfactant template is the best example for soft template (Zhao and Wang, 2012). Herein, surface of surfactant micelles with a particular shape are covered by polymer chains to form the template (Mantilaka *et al.*, 2014). The nanoparticles of inorganic material are fabricated on the surface of polymer. After washing, surfactants are removed from the system (Zhao and Wang, 2012). However, sometimes, polymer remains in the final product. Therefore, polymer must be selected based on the purpose and final product. For example, calcium carbonate hollow structures are fabricated on surfactant/polymer templates (Zhao and Wang, 2012). After the synthesis, the material can be heated at 500 °C in order to combust the polymer since calcium carbonate is very stable at this temperature (Mantilaka *et al.*, 2014). However, if the polymer is not affective to the final product, no need to put any effort to remove it from the product.

The end use of these hollow materials depends on their particle size, shape (morphology) and volume of hole (Mantilaka *et al.*, 2014). Therefore, there are many efforts on synthesis of various shapes of hollow inorganic materials. The shape of the final particle and the hole depend on the shape of the template. Recently, we, at the physical chemistry research laboratory, Department of Chemistry, University of Peradeniya, have invented and reported a novel nanostructured hollow calcium carbonate material which has morphology, similar to a bone (Mantilaka *et al.*, 2014). So it was named hollow-bone-like calcium carbonate. The SEM and TEM images of the material which has been synthesized are depicted in Figure 03. This structure has been formed by fabricating amorphous and calcite (a crystalline form of calcium carbonate) nanoparticles on anionic polymer/cationic surfactant template. It is expected to use this material for anticancer drug delivery in the future.

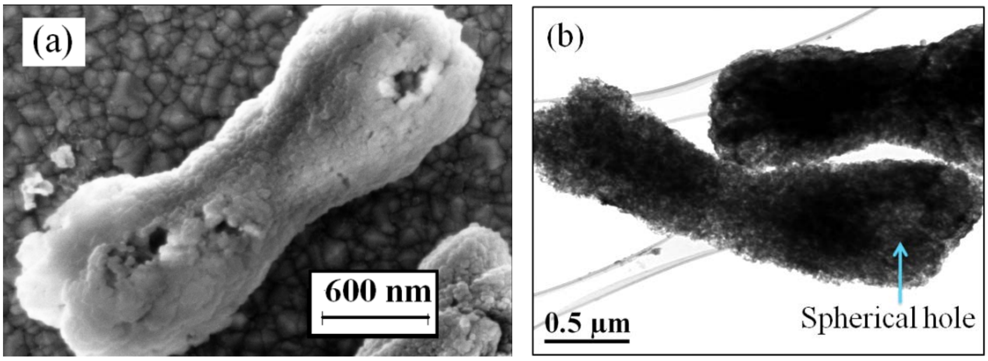

Figure 03: (a) SEM image and (b) TEM image of nanostructured hollow-bone-like calcium carbonate micro-particles which was synthesized at Physical chemistry Research Laboratory, Department of Chemistry, University of Peradeniya

References:

Hou, Q., Tao, X., Yang, Y.J. and Ma, Y. (2010). Optimal synthesis of mesostructured hollow titania nanotubes template on $CaCO_3$ nanoparticles. *Powder Technology,* 198, 429–434.

Liu, W.N., Ding, D., Song, Z.L., Bian, X., Nie, X.K., Zhang, X.B., Chen, Z. And Tan, W. (2014). Hollow graphitic nanocapsules as efficient electrode materials for sensitive Hydrogen peroxide detection. *Biosensors and Bioelectronics*, 58, 438-444.

Mantilaka, M.M.M.G.P.G., Pitawala, H.M.T.G.A., Rajapakse, R.M.G., Karunaratne, D.G.G.P., Wijayantha, K.G.U. (2014). Formation of hollow bone-like morphology of calcium carbonate on surfactant/polymer templates. *Journal of Crystal Growth,* 392, 52-59.

Zhao, H., Li, Y., Liu, R., Zhao, F., Hu, Y. (2008). Synthesis method for silica needle-shaped nano-hollow structure. *Materials Letters,* 62, 3401–3403.

Zhao, L., Wang, J. (2012). Biomimetic synthesis of hollow microspheres of calcium carbonate crystals in the presence of polymer and surfactant. *Colloids and Surfaces A,* 393, 139–143.