J. Indian Chem. Soc.,
Vol. 85, February 2008, pp. 182-183

Synthesis of hollow microsphere containing of cavity

N. Venkatathri*

Composite Materials Center, Korea Institute of Ceramic Engineering & Technology, 233-5, Gasan-Dong, Guemcheon-Gu, Seoul 153-801, South Korea

E-mail : venkatahrin@yahoo.com

Manuscript received 28 March 2007, revised 1 August 2007, accepted 6 November 2007

Abstract : A novel procedure is reported for hollow silica microsphere containing cavity. Reaction with polystyrene, water, cetyltrimethylammonium chloride and tetraethylorthosilicate at room temperature give silica hollow microsphere containing cavity. Initially polystyrene synthesis was achieved by dispersion polymerization. Calcinations will eliminate the organics and leave microsphere as hollow. Scanning electron micrograph was used to identify the morphology.

Keywords : Polystyrene, silica microsphere, cavity, SEM.

Introduction

Nanometer to micrometer sized materials are widely used in different areas of process industries. There are several research focused on the preparation of hollow microspheres. This is an important class of materials science having applications in the field of delivery of encapsulated products for cosmetic and medical purposes to their use as lightweight composite materials and as fillers with low dielectric constant in electronic components[1]. Applications for hollow microspheres also cover areas such as catalysis, acoustic insulation, piezoelectric transducers and manufacture of advanced materials[2]. Various materials have been used for the preparation of hollow microspheres, for example, polymers, glasses, metals and ceramics[1]. The methods currently used to fabricate a wide range of stable hollow spheres include nozzle reactor processes, emulsion/phase separation, sol-gel processing and sacrificial core techniques[1]. The latter involves the use of cores that are coated with the material interest. The core is subsequently dissolved or volatilized by heating, leaving the shell of the desired hollow microsphere.

The fabrication of hollow spheres has been greatly impacted by the layer by layer (LbL) self assembly technique. This method allows the construction of composite multilayer assemblies based on the electrostatic attraction between nanoparticles and oppositely charged polyions[3-9]. An important extension of the method is the preparation of multilayers of colloids on three dimensional substrates. For example, polystyrene beads were coated with homogeneous layers of colloidal silica particles[10]. LbL coated colloidal spheres of 640 nm comprising layers of titania or silica were used for the preparation of macroporous structures[11].

In the present study, the polystyrene suspension and cetyltrimethylammonium chloride and tetraethylorthosilicate were employed for the preparation of hollow micro structures. Polystyrene sphere were synthesized by using potassium persulfate initiator.

Experimental

Synthesis of polystyrene sphere template :

Polystyrene sphere suspension was prepared by dispersion polymerization in water with potassium per sulfate as initiator. The apparatus for the polymerization consisted of a 250 mL three necked round bottomed flask, equipped with a mechanical stirrer, a condenser and connection with a nitrogen reservoir. The monomer solution was prepared by mixing 20 ml of styrene with 78 ml of water in the flask at 343 K. Potassium per sulfate (2 g) was dissolved in the above monomer solution. Polymerization was carried out under nitrogen pressure by stirring (350 rpm) the mixture solution at the temperature 343 K for 4 h. The resulting polystyrene suspension was centrifuged and the residue and extract were collected separately and as it was found some of the polystyrene was present in extract and it was used separately for silica capsule preparation. The dried residue has uniform spherical shape with an average diameter 300–500 nm (Fig. la).

*Present address : Department of Chemistry, Anna University, Chennai-600 025, India

Synthesis of silica capsules :

Silica species are hydrolyzed and oligomerized over the cylindrical micelle arrays to form silica coated polymer core composites. The reaction mixture was prepared by mixing 34.4 ml tetraethylorthosilicate (98%, Aldrich, USA), cetyltrimethylammoniumchloride (3.96 ml, CTACl, 25%, Aldrich, USA) and polystyrene suspension (90 ml, 4.8%) in the polyethylene bottle at 298 K and stirred vigorously for 24 h. The resulting solids were collected by centrifugation, washed with ethanol-water (1 : 1 v/v) mixture solution and dried at 333 K for 12 h. Surfactant micelles were partly removed by washing with 0.1 *M* HCl-EtOH, filtering and drying in an oven. The rest of surfactant and polystyrene spheres were completely removed by subsequent calcinations in air at 823 K for 8 h at a heating rate of 1.5 K/min to obtain hollow core silica capsules.

The particle size and shape were analyzed by a Topcon, SM-300 scanning electron microscope. The copper disc pasted with carbon tape and the sample was dispersed over the tape. The disc was coated with gold in ionization chamber before microscopic analysis.

Results and discussion

The scanning electron microscopic picture of polystyrene residue (Fig. 1a) shows that it is having sphere morphology with 200–800 nm particle size. The microsphere obtained from polystyrene extract is having sphere shape with 2–8 μm particle size (Fig. 1b). The hollow microsphere containing cavity obtained from polystyrene residue having spherical morphology contain 18 μm particle size with 10 μm hollow size (Figs. 1c,d).

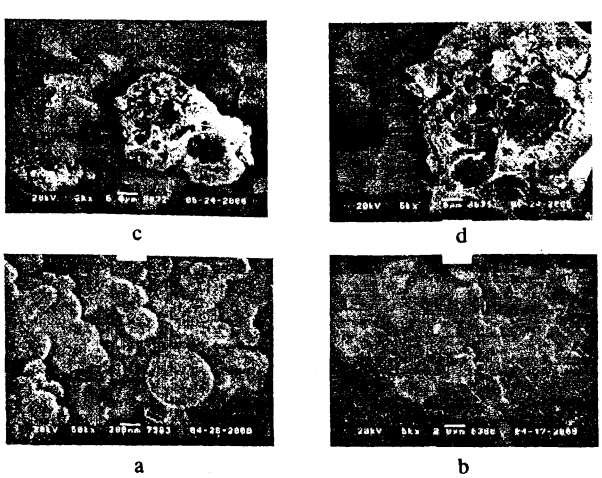

Fig. 1. SEM picture of (a) polystyrene residue, (b) silica microsphere obtained from polystyrene extract, (c) hollow silica macrosphere from polystyrene residue and (d) hollow silica macrosphere picture (c) with magnified scale.

The schematic representation of preparation of silica hollow microsphere containing cavity shows that first polystyrene sphere getting agglomerated, to the agglomerated polystyrene, surfactant are surrounded. Silica layers are formed over surfactant layers which gives silica microsphere. Within silica layer further cavities are formed. On calcinations the polystyrene agglomerates and surfactants are removed and the hollow sphere and cavities are left out.

Conclusion :

In this work, the hollow silica micro sphere with cavity was formed. On calcinations the polystyrene core and surfactant shell were eliminated and silica shell remains intact. The micro structured shells were synthesized by templating polystyrene latex spheres, which could assist synergistic self-assembly between surfactant molecules and silicates to form mesoscopically ordered composite shells on the latex spheres. Silicate species and the surfactant micelles self assembled to form micro porous shell structures on the surface of the PS latex spheres.

Acknowledgement

The author N.V. thanks Brain Pool Program, South Korea and Council of Scientific and Industrial Research, New Delhi, India for a fellowship.

References

1. D. L. Wilcox, M. Berg, T. Bernat, D. Kellerman and J. K. Cochran, (eds.) "Hollow and Solid Spheres and Microspheres : Science and Technology Associated with their Fabrication and Application", Mater. Res. Soc. Pro., 1995, 372.
2. F. Caruso, *Chem. Eur. J.*, 2000, **6**, 413.
3. G. Decher, *Science*, 1997, **277**, 1232.
4. R. K. Iler, "The Chemistry of Silica", John Wiley and Sons, Chichester, UK, 1979.
5. Y. Lvov, K. Ariga, I. Ichinose and T. Kunitake, *J. Am. Chem. Soc.*, 1995, **117**, 6117.
6. G. Decher, B. Lehr, K. Lowack, Y. Lvov and J. Schmitt, *Biosens. Bioelectron.*, 1994, **9**, 677.
7. K. Araki, M. J. Wagner and M. S. Wrighton, *Langmuir*, 1996, **16**, 5393.
8. V. Tsukruk, F. Rinderspacher and A. Bliznyuk, *Langmuir*, 1997, **13**, 2171.
9. E. R. Kleinfield and G. S. Ferguson, *Science*, 1994, **265**, 370.
10. F. Caruso, R. A. Caruso and H. Mohwald, *Science*, 1998, **282**, 1111.
11. D. Wang, R. A. Caruso and F. Caruso, *Chem. Mater.*, 2001, **13**, 364.