

# Template-Free Single-Step Room-Temperature Fabrication of Metal Oxide Hollow Nanospheres and Nanofoams

Xingmao Jiang<sup>\*</sup>, Jianzhong Min<sup>\*</sup>, Angela L. Triplett<sup>\*\*</sup> and C. Jeffrey Brinker<sup>\*\*\*</sup>

<sup>\*</sup> Changzhou University, School of Petrochemical Engineering, 213164, PR China, jxm@cczu.edu.cn

<sup>\*\*</sup> University of New Mexico, Departments of Molecular Genetics and Microbiology, USA

<sup>\*\*\*</sup> The College of Wooster, Department of Physics, Wooster OH 44691, USA

## ABSTRACT

Metal oxide hollow nanospheres and nanofoams are fabricated at room temperature by a single-step template-free aerosol process using low boiling-point hydrophobic solvent by controlling mass transport and sol-gel reactions at droplet interface. The facile technique is important for drug delivery, wave absorption, catalysts, sensors and energy storage.

**Keywords:** aerosol, hollow sphere, diffusion, evaporation, interface reaction

Hollow nanospheres and nanofoams possess characteristics such as low density, high surface area and adjustable refractive index that make them attractive to tune their mechanical, optical, electrical, and chemical properties for applications ranging from drug and gene delivery [1,2,3], catalysts[4], antireflective coatings[5,6], and wave absorbing, energy storage and supercapacitor[7], low dielectric constant substrates[8], chemical and biological sensing, labeling, and early detection of cancer[9,10], metamaterials[11], optoelectronics[12], and photo-voltaics [13]. For example, encapsulation/control release of enzyme, vaccine, peptide and DNA, fluorescent and field-responsive agents has been exploited for treatment of various diseases. Ceramics are biocompatible and have excellent thermal and chemical stability[14]. Encapsulation of drugs in metal oxide nanoparticles is advantageous in maintaining the stability of nanocapsule suspensions after oral or parenteral administration[15]. Vapor-solid interfacial reactions such as laser ablation, molecular beam epitaxy, and chemical vapor deposition have been applied for fabrication of hollow and core/shell structured nanospheres[16]. Hollow metal, metal sulfide, and metal oxide spheres have been synthesized by self-assembly in the presence of hard and soft templates[17,18,19,20]. However, most often the template cores are difficult to remove for contamination-free hollow structures. Hollow spherical indium and ZnS have been synthesized at high temperature via a template-free solvothermal route[21,22]. Metal oxide hollow nanospheres have been made by thermal decomposition and subsequent surface gellation via aerosol pyrolysis starting from hydrophilic solvent based precursors[23,24]. The high-temperature methods can not be used for encapsulation of heat sensitive drugs. Two-fluid nozzle, microfluid channels, gas-blowing, and acoustic cavitation have been used only for macro- and microscale hollow structures due to the high-pressure pumping and easy clogging problems[25,26,27,28].

Sol-gel technique combined with emulsion and water extraction has been used to prepare hollow metal oxides[29]. Hollow TiO<sub>2</sub> particles of tens of micrometers in diameter have been prepared by spraying water droplets into titanium tetraisopropoxide (TTIP) solution[30]. The above methods can not be applied for sub-micro hollow structures due to high water concentration in the droplets and fast water mass transport. There are urgent needs for facile, low-temperature, low-cost, template-free, nondestructive fabrication methods for nanospheres and nanofoams.

We fabricated hollow nanospheres and nanofoams by synergically controlling the phase equilibrium, mass transport and sol gel kinetics at droplet interface. The process started with an anhydrous homogeneous metal alkoxide solution in hexane. The molar ratios for TTIP or tetraethyl orthogermanate to hexane were kept as 0.14:1. Aerosol droplets were generated at room temperature using a 9302A atomizer (TSI Inc) with 20 psi dry nitrogen as the atomization gas. Low viscosity and surface tension of hexane enables small droplet size. The aerosol stream was induced into a two-foot long tube kept at room temperature and saturated with 28% ammonia solution. Hollow nanospheres were collected on a filter paper or TEM grids.

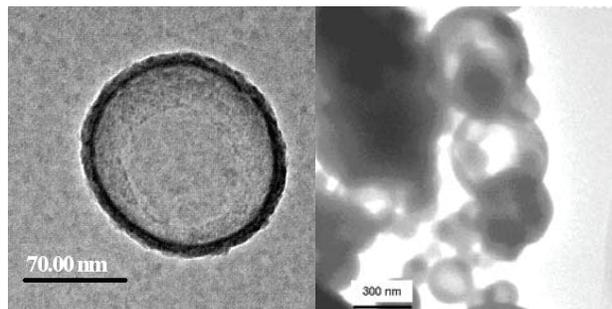


Figure 1: TEM images of hollow spherical particles: (a) inset is hollow spherical titania; (b) hollow spherical GeO<sub>2</sub>.

Figure 1 shows representative TEM images for TiO<sub>2</sub> and GeO<sub>2</sub> hollow nanospheres. When the aerosol droplets were sprayed directly onto 28% ammonia solution. A transparent film of metal oxide nanofoam floating on the surface of the solution was generated. Partially dried and consolidated droplets aggregate into titania nanofoam before the sol-gel reaction and solvent evaporation were complete.

Figure 2 shows representative TEM image for TiO<sub>2</sub> nanofoam.

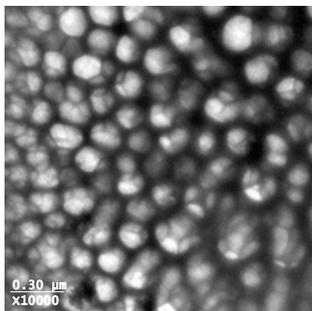


Figure 2: TEM images of titania nanofoam

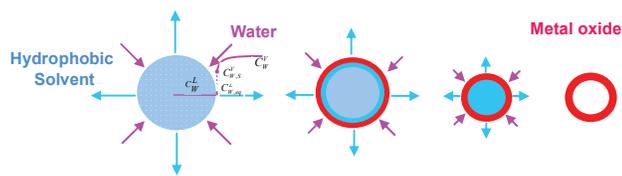


Figure 3: Schematic illustration of the mechanism for the fabrication of hollow spherical structures by evaporation induced self-assembly.

The formation mechanism for the hollow structures is described as shown in Figure 3. Quick evaporation of the solvent generates steep concentration gradients for metal oxide precursor in the droplet and for vapor phase water near droplet surface. Solvent evaporation dilutes vapor phase water concentration,  $C_{w,s}^v$  near droplet surface. The water solubility in the droplet near the surface,  $C_{w,s}^l$  is defined as the  $C_{w,s}^v$  divided by a very high Henry coefficient for water in hexane, limiting the driving force for water transport across the droplet surface and inside sol-gel reactions. Rapid hydrolysis of the highly reactive precursors under catalytic vapor (HCl or NH<sub>3</sub>) consumes timely diffused water and keeps the sol-gel reactions happen only near droplet surface. Quick evaporation of solvent causes a temperature depression at the droplet surface, and the nucleation happens only near droplet surface. The growing oxide shell serves as the transport barrier for further water diffusion. The sol gel reactions deplete all the precursor in the droplets, leaving behind a well defined oxide hollow structure with a thin shell. The hollow nanostructure is controlled by the initial droplet size, precursor compositions, solvent volatility, processing temperature, residence time, and vapor phase water and catalyst concentrations. For room-temperature fabrication within short residence time, fast sol-gel kinetics and low boiling point solvent are necessary to make the hollow structures. Hollow structures of multiple metal oxides can be fabricated using binary or ternary metal oxide precursors. For less reactive precursors, the metal oxide precursor molecules react with unreacted diffused water inside the droplets. A catalytic HCl or NH<sub>3</sub> vapor is required to catalyze the sol gel reactions to enable the hollow structures. If the vapor phase

humidity is too high, the solvent is less volatile and less hydrophobic, or the precursor is less reactive, excessive unreacted water will diffuse inward and react with the precursor molecules inside the droplets, favoring formation of solid particles. Caffeine was encapsulated as a model hydrophobic drug in titania capsules with high encapsulation efficiency by spraying TTIP-caffeine-methylene chloride droplets at room temperature[31]. The method is promising especially for heat sensitive and hydrolysable hydrophobic drugs. It is expected that hydrophobic magnetic nanoparticles and quantum dots can be dispersed in the hydrophobic precursors to form multifunctional hollow nanostructures. Similarly, hollow metal sulfide or halide nanospheres and nanofoams can be fabricated by spraying hydrophobic precursor droplets into H<sub>2</sub>S or HCl instead of H<sub>2</sub>O vapor. It is expected hollow metal nanospheres can be made after further reduction of the sulfide or halide hollow nanospheres[32].

In summary, we demonstrate a facile, general fabrication method for hollow nanospheres and nanofoams. The hollow structures can be engineered by the aerosol generation conditions. The template-free, room-temperature, single step, low-cost aerosol process is continuous and easy to scale-up. We have developed computer codes to quantitative describe vapor-liquid equilibrium and coupled mass and heat transport of multicomponent droplet evaporation under moving boundary conditions[33,34,35]. Sol-gel kinetics will be incorporated into the codes to quantitatively understand the process and optimize the fabrication conditions for the hollow nanostructures.

This work was supported by Key Laboratory of Fine Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology and PAPD of Jiangsu Higher Education Institutions.

## REFERENCES

- [1] H. Cohen, R.J Levy, J. Gao, I. Fishbein, V. Kousaev, S. Sosnowski, S. Slomkowski and G. Golomb, *Gene Ther*, 7, 1896-1905, 2000.
- [2] M. Aboubakar, F. Puisieux, P. Couvreur, M. Deyme and C. Vauthier, *J. Biomed. Mater. Res*, 47, 568-576, 1999.
- [3] H. Ai, S. A. Jones, M. M. de Villiers and Y. M. Lvov, *J. Control Release*, 86, 59-68, 2003.
- [4] X. W. Lou, L. A. Archer and Z. C. Yang, *Adv. Mater*, 20, 3987-4019, 2008.
- [5] Z.C. Sun, F. Bai, H. M. Wu, S. K. Schmitt, D. M. Boye, H. Y. Fan, *J. Am. Chem. Soc*, 131, 13594-13595, 2009.
- [6] W. Wei, H. F. Cheng, Z. Y. Chu, Z. H. Chen, Y. J. Zhou, *J. Inorg. Mater*, 24, 320-324, 2009.
- [7] M. Xu, L. Kong, W. Zhou, *J. Phys. Chem. C*, 111, 19141-19147, 2007.
- [8] F. Caruso, *Chem-Eur. J*, 6, 413-419, 2000.
- [9] D.K. Yi, S. T. Selvan, S. S. Lee, G. C. Papaefthymiou, D. Kundaliya and J. Y. Ying, *Nano Lett*, 127, 4990-4991, 2005.

- [10] N. Gaponik, I. L. Radtchenko, M. R. Gerstenberger, Y. A. Fedutik, G. B. Sukhorukov and A. L. Rogach, *Nano Lett*, 3, 369-372, 2003.
- [11] A. Boardman, M. Brongersma, M. Stockman, and M. Wegener, *J. Opt. Soc. Am. B*, 26, PM1-PM1, 2009.
- [12] K. J. Major, C. De, S. O. Obare, *Plasmonics*, 4, 61-78, 2009.
- [13] K. L. Knappenberger, A. M. Schwartzberg, A. M. Dowgiallo, C. A. Lowman, *J. Am. Chem. Soc*, 131, 13892-13893, 2009.
- [14] S. Areva, H. Paldan, T. Peltola, T. Narhi, M. Jokinen and M. Linden, *J. Biomed. Mater. Res-A*, 70, 169-178, 2004.
- [15] R. Pohlmann, V. Weiss, O. Mertins, N. P. da Silveira and S. S. Guterres, *Eur. J. Pharm. Sci*, 16, 305-312, 2002.
- [16] C. R. Xiong, D. Coutinho and K. J. Balkus, *Micropor. Mesopor. Mater*, 86, 14-22, 2005.
- [17] A.D. Dinsmore, M. Nikolaides, M. Hsu, A.R. Bausch and D.A. Weitz, *Science*, 298, 1006-1009, 2002.
- [18] F. Caruso, R. A. Caruso and H. Mohwald, *Science*, 282, 1111-1114, 1998.
- [19] Y. D. Xia and R. Mokaya, *J. Mater. Chem*, 15, 3126-3131, 2005.
- [20] S. Chah, J. H. Fendler, J. Yi, *J. Colloid Interf. Sci*, 250, 142-148, 2002.
- [21] H. J. Liu, Y. H. Ni, M. Han, Q. Liu, Z. Xu, J. N. Hong and X. Ma, *Nanotechnology*, 16, 2908-2912, 2005.
- [22] V. Jokanovic, A. M. Spasic and D. Uskokovic, *J. Colloid Interf. Sci*, 278, 342-352, 2004.
- [23] P. Tartaj, T. Gonzalez-Carreno and C. J. Serna, *Adv. Mater*, 13, 1620-1624, 2001.
- [24] G. L. Messing, S. C. Zhang and G. V. Jayanthi, *J. Am. Ceram. Soc*, 76, 2707-2726, 1993.
- [25] G. Loscertales, A. Barrero, I. Guerrero, R. Cortijo, M. Marquez and A. M. Ganan-Calvo, *Science*, 295, 1695-1698, 2002.
- [26] N. K. Kim, K. Kim, D. A. Payne, et al., *J. Vac. Sci. Technol. A*, 7, 1181-1184, 1989.
- [27] X. Q. Gong, L. M. Wang and W. J. Wen, *Chem. Comm*, 31, 4690-4692, 2009.
- [28] J. H. Kim, W. C. Choi, H. Y. Kim, Y. Kang, Y. K. Park, *Powder Technol*, 153, 166-175, 2005.
- [29] J. G. Liu and D. L. Wilcox, *J. Mater. Res*, 10, 84-94, 1995.
- [30] S. Nagamine, A. Sugioka and Y. Konishi, *Mater. Lett*, 61, 444-447, 2007.
- [31] X. M. Jiang and C. J. Brinker, *Hollow Spherical Metal Oxides*, US Patent 7,744,673.
- [32] Haruo Kobayashi and Carl Wagner, *Investigations on the Reduction of Silver Sulfide and Cuprous Sulfide by Hydrogen*, *J. Chem. Phys*, 26, 1609-1614, 1957.
- [33] X.M. Jiang, "Engineering of Aerosol Nanoparticle Architectures," Ph.D. Dissertation, University of New Mexico, 2006.
- [34] C. J. Homer, X. M. Jiang, T. L. Ward, C. J. Brinker and J. P. Reid, *Phys. Chem. Chem. Phys*, 11, 7780-7791, 2009.
- [35] X. M. Jiang, T. L. Ward, F. van Swol, and C. J. Brinker, *Ind. Eng. Chem. Res*, 46, 3019-3021, 2010.