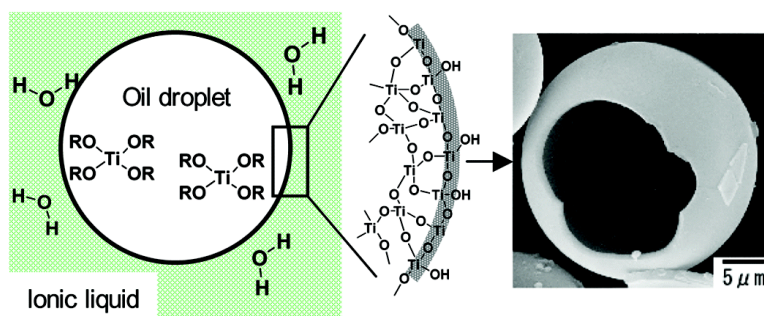


Interfacial Synthesis of Hollow TiO₂ Microspheres in Ionic Liquids

Takuya Nakashima, and Nobuo Kimizuka

J. Am. Chem. Soc., **2003**, 125 (21), 6386-6387 • DOI: 10.1021/ja034954b • Publication Date (Web): 06 May 2003

Downloaded from <http://pubs.acs.org> on March 28, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 67 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Interfacial Synthesis of Hollow TiO₂ Microspheres in Ionic Liquids

Takuya Nakashima and Nobuo Kimizuka*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581, Japan

Received March 2, 2003; E-mail: kimitcm@mbox.nc.kyushu-u.ac.jp

We describe herein a single-step synthesis of hollow titania microspheres in ionic liquids, which can be simultaneously modified with gold nanoparticles and dye carboxylate molecules. It gives a simple and general route to the design of functional organic/inorganic hollow capsules.

Room-temperature ionic liquids are receiving much attention as environmentally benign solvents for organic chemical reactions,¹ separations,² and for electrochemical applications.³ Recent developments include their use for biopolymers^{4,5} and molecular self-assemblies.^{4,6} They are nonvolatile, thermally stable and display limited miscibility both with water and with common organic solvents. In contrast to their successful applications in organic or materials chemistry, their use in inorganic synthesis is still in its infancy. To our knowledge, the use of ionic liquids as solvents for the inorganic synthesis has been limited to the acid-catalyzed sol-gel synthesis of silica aerogels⁷ and formation of palladium⁸ or iridium⁹ nanoparticles. Here we describe a first example of the synthesis of hollow, metal oxide microspheres and their simultaneous chemical modification in ionic liquids.

1-Butyl-3-methylimidazolium hexafluorophosphate ([C₄mim]PF₆) was synthesized according to the literature.² The amount of water adsorbed from the atmosphere was ca. 0.1 wt % (ca. 80 mM) as determined by the Karl Fischer's method. Into a 10-mL screw vial, was placed 1.8 mL of [C₄mim]PF₆, and 0.2 mL of anhydrous toluene solution containing 0.2 M Ti(OBu)₄ was added under vigorous stirring. After the translucent mixture stirred for 10 min, methanol (3 mL) was added, and the diluted mixture was centrifuged at 1000 rpm for 10 min. The titania gels obtained were corrected by filtration and were dried in vacuo.

Figure 1 shows scanning electron micrographs (SEM, Hitachi S-5000) of the titania gels prepared at the stirring rate of 1000 rpm. Microspheres with diameters of 3–20 μm are observed, with a very small number of mechanically fractured particles depicted in the inset. Apparently, the particles possess hollow structures, and the wall thickness observed is ca. 1 μm. Although the microspheres display size distribution,¹⁰ their average size is controllable, depending on the experimental conditions. At the stirring rate of 700 rpm, larger microspheres are formed (diameter, 5–50 μm), whereas spheres were scarcely formed at the lower stirring rate of 400 rpm. In addition, the average diameter of the microspheres is also dependent on the reaction temperature: 8.8, 10.8, and 14.0 μm at 15, 25, and 45 °C, respectively.

Scheme 1 illustrates the mechanism for the hollow microsphere formation. Because of the limited miscibility of toluene with the ionic liquid, micro-sized droplets are formed under vigorous stirring. The formation of smooth, hollow titania microspheres in Figure 1 clearly indicates that Ti(OBu)₄ molecules in the microdroplet are hydrolyzed selectively at the interface. When the longer-chained alkyl [C₈mim]BF₄ is employed, hollow particles were similarly obtained. The water content in the ionic liquid must be small, since

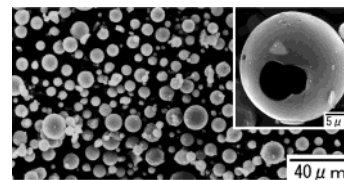
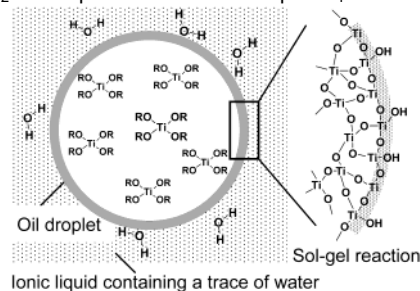


Figure 1. SEM images of hollow TiO₂ gel microspheres prepared in the ionic liquid. The inset shows a fractured sample.

Scheme 1. Schematic Illustration of the Formation Process of Hollow TiO₂ Microspheres at the Oil Droplet/C₄mim Interface



doping of 2 wt % water in [C₄mim]PF₆ caused formation of rough, irregular titania microparticles.

To date, hollow SiO₂ microspheres have been prepared by the interfacial sol-gel reaction of tetraethoxysilane in surfactant-stabilized oil/water emulsions¹¹ or by the use of nozzle-reactor methods (spray drying).¹² Alternatively, sacrificial templates such as aqueous micelles,¹³ polyelectrolyte aggregates¹⁴ and colloid particles¹⁵ have been employed. However, the presence of bulk water in these sacrificial approaches hampers their application to the more reactive metal alkoxides. Hollow TiO₂ microspheres have been prepared by the spray-drying technique¹⁶ or by the time-consuming layer-by-layer absorption of polyelectrolyte and titanium complexes on colloid particles.¹⁷ The latter technique requires succeeding removal of the sacrificial cores by calcination or chemical etching.¹⁷ A highly desirable goal in the synthesis of functional hollow spheres is a single-step reaction for the reactive metal alkoxides, without the use of sacrificial core materials.

It is noteworthy that the hollow titania gel microspheres are obtainable in one step without the use of surfactants and they are stably suspended without coagulation. The specimens after centrifugation displayed IR peaks at 2957–2871 and 1560, 1460, 1130 cm⁻¹, which are assigned to the aliphatic C–H stretching and ring stretching of C₄mim⁺ molecule, respectively. Therefore, C₄mim⁺ molecules are adsorbed to the surface of hollow microspheres possibly by the electrostatic interaction and maintaining their suspensibility in the ionic liquid. Importantly, the present technique was also applicable to the other reactive metal oxides such as Zr(OBu)₄, Hf(OBu)₄, Nb(OBu)₅, and InSn₃(OR)_x (GELEST Co. Ltd.), and hollow microspheres were similarly obtained for a variety of reactive metal alkoxides.

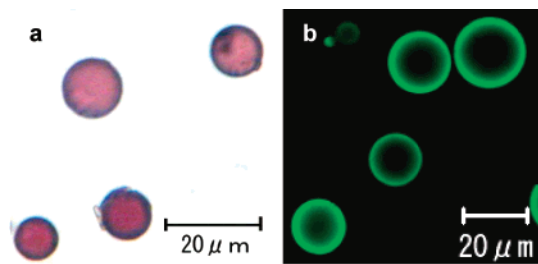


Figure 2. (a) Differential interference contrast micrograph of TiO_2 microspheres containing gold nanoparticles. (b) CLSM image of TiO_2 microspheres whose shells were doped with FITC.

We then investigated simultaneous modifications of the micro-particles with metal nanoparticles and with functional organic molecules. When dodecanthiol-passivated gold nanoparticles (average diameter, 9 nm) and $\text{Ti}(\text{OBU})_4$ are dissolved in the toluene phase (concentration, gold nanoparticle; 0.5 mg mL^{-1} , $\text{Ti}(\text{OBU})_4$; 100 mM), brown hollow microspheres of titania were obtained. The color is maintained even after repeated washing of the sample with toluene, which is a good solvent for the gold nanoparticles. Figure 2a shows differential interference contrast microscopy of the obtained microspheres. The purple color indicates the presence of gold nanoparticles, and the presence of Au atoms was also confirmed by energy-dispersive X-ray (EDX) spectroscopy. Transmission electron microscopy of the microtomed sample showed the Au nanoparticles buried in the shells.

Carboxylic acids are known to coordinate to titania gels,^{18,19} and we then employed tetraphenylporphyrin tetracarboxylic acid, ferrocene carboxylic acid, and fluorescein isothiocyanate (FITC) as the dopants. When these organic carboxylic acids are mixed with $\text{Ti}(\text{OBU})_4$ in *n*-butanol/toluene (1/9 by vol) and the mixture was vigorously mixed with the ionic liquid, colored microspheres are obtained in all cases. Figure 2b displays confocal laser scanning microscopy (Carl Zeiss, LSM 510) of the titania microspheres containing FITC. Emission from FITC was observed from the shells of microspheres. Fluorescence spectra obtained from Figure 2b showed an emission peak at 530 nm, which is red-shifted compared to that of molecularly dispersed FITC (520 nm) in butanol/toluene (10/90 by vol). The observed red-shift is typical for the FITC with its carboxylate group coordinated to TiO_2 gels.¹⁹

The nondoped titania gel microspheres were then calcined at 500 °C for 5 h. Thermogravimetric (TG) analysis of the hollow microspheres showed the weight loss of ca. 34% due to removal of the surface-bound ionic liquids and the remaining butoxide groups, as confirmed by IR spectra. The hollow capsule structure was maintained even after calcination. The hollow gel before calcination shows no X-ray diffraction peak, indicating that the gel is amorphous. On the other hand, the calcined microspheres displayed crystalline reflection peaks that are characteristic to the anatase TiO_2 .²⁰

In conclusion, we have developed an ionic liquid-based, simple synthesis of hollow, metal oxide microspheres. The significance of the present study is 4-fold. First, the interfacial sol-gel reaction in ionic liquids provides an efficient, one-step route to the inorganic hollow microspheres. The size of hollow spheres can be controlled

by physical conditions such as stirring rate and temperature. Imidazolium molecules act not only as the solvent but also as stabilizers for the hollow microspheres. Second, anatase microspheres of TiO_2 are stably obtained after calcination. Third, this technique is widely applicable to the reactive metal alkoxide precursors. Fourth, the hollow titania gels can be simultaneously modified with functional carboxylic acids and metal nanoparticles. These features make the interfacial sol-gel synthesis in ionic liquids a versatile and general route to the functional inorganic microspheres. We envisage that the asymmetric modification of the inner and outer surfaces of TiO_2 microspheres with photofunctional molecules and metal colloids may lead to a new family of photocatalytic systems.

Acknowledgment. The present work is supported by a Grant-in-Aid for Scientific Research (B) (No. 13440210) from Japan Society for the Promotion of Science. We thank Professor A. Takahara and Mr. K. Yamamoto (Kyushu University) for the use of a Rigaku RINT-2500 diffractometer. We also thank Professor I. Hamachi (Kyushu University) for the use of the Carl Zeiss LSM 510.

Supporting Information Available: SEM images of hollow titania spheres prepared at different conditions, electron microscopy of the microtomed hollow titania spheres containing gold nanoparticles, and X-ray diffraction patterns of hollow microspheres before and after the calcination (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) For recent reviews, see: (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (b) Sheldon, R. *Chem. Commun.* **2001**, 2339.
- (2) Huddleston, J. G.; Willauer, H. D.; Swatoski, R. P.; Visser, A. E.; Rogers, R. D. *Chem. Commun.* **1998**, 1765.
- (3) (a) McEwen, A. B.; McDevitt, S. F.; Koch, V. R. *J. Electrochem. Soc.* **1997**, *144*, L84. (b) Dickinson E. V.; Williams M. E.; Hendrickson, S. M.; Masui, H.; Murray, R. W. *J. Am. Chem. Soc.*, **1999**, *121*, 613.
- (4) Kimizuka, N.; Nakashima, T. *Langmuir*, **2001**, *17*, 6759.
- (5) Swatoski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. *J. Am. Chem. Soc.* **2002**, *124*, 4974.
- (6) Nakashima, T.; Kimizuka, N. *Chem. Lett.* **2002**, 1018.
- (7) Dai, S.; Ju, Y. H.; Gao, H. J.; Lin, J. S.; Pennycook, S. J.; Barnes, C. E. *Chem. Commun.* **2000**, 243.
- (8) Deshmukh, R. R.; Rajagopal, R.; Srinivasan, K. V. *Chem. Commun.* **2000**, 1544.
- (9) Dupont, J.; Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P.; Teixeira, S. R. *J. Am. Chem. Soc.* **2002**, *124*, 4228.
- (10) The stirring rate was roughly controlled by using a magnetic stirrer and a small stirrer chip. Due to the high viscosity of the ionic liquid, nonuniform mixing may lead to the observed size distribution.
- (11) Schacht, S.; Huo, Q.; Voigt-Martin, I. G.; Stucky, G. D.; Schuth, F. *Science* **1996**, *273*, 768.
- (12) Bruinsma, P. J.; Kim, A. Y.; Liu, J.; Baskaran, S. *Chem. Mater.* **1997**, *9*, 2507.
- (13) Flower, C. E.; Khushalani, D. Mann, S. *Chem. Commun.* **2001**, 2028.
- (14) van Bommel, K. J. C.; Jung, J. H.; Shinkai, S. *Adv. Mater.* **2001**, *13*, 1472.
- (15) Caruso, F.; Caruso, R. A.; Mohwald, H. *Science* **1998**, *282*, 1111.
- (16) Iida, M.; Sasaki, T.; Watanabe, M. *Chem. Mater.* **1998**, *10*, 3780.
- (17) Caruso, F.; Shi, X.; Caruso, R. A.; Susha, A. *Adv. Mater.* **2001**, *13*, 740.
- (18) (a) Roger, C.; Hampden-Smith, M. J. *J. Mater. Chem.* **1992**, *2*, 1111. (b) Lee, S.-W.; Ichinose, I.; Kunitake, T. *Langmuir* **1998**, *14*, 2857.
- (19) Ichinose, I.; Kunitake, T. *Chem. Lett.* **2001**, 626.
- (20) The surface of calcined, TiO_2 hollow spheres can be also modified with FITC, by mixing them in butanol/toluene as confirmed by CLSM.

JA034954B