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A Facile Reprecipitation Method for the Preparation of Polyimide Hollow Spheres with Controllable Morphologies and Permeable Shell

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We present our preliminary work on the fabrication of polyimide hollow sphere by reprecipitation. Through fine-tuning the PAA concentration, many intriguing shapes, including deflated capsules, bowl-shaped and dimple-like hollow spheres can be obtained. Adding salt to the PAA solution helps the formation of PI hollow spheres with complete shells. The morphologies can be fixed through imidization, thus obtaining a controllable and reproducible method to prepare high-performance polyimide hollow spheres with various morphologies.

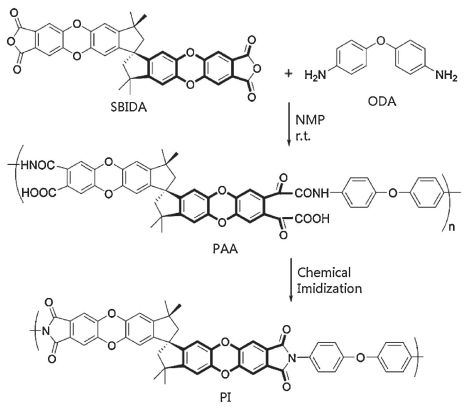
The fabrication of hollow spheres with controllable morphologies has attracted great attention in recent decades, because these materials have protected porous cores which are suitable for encapsulating a large variety of substances and thus have great potential for applications such as catalysts, low-dielectric fillers, adsorbents, and drug storage and delivery carriers.[1–6] A variety of hollow spheres which consist of metals, ceramics, or polymers have been reported, and the approaches can be generally divided into two categories on the basis of the properties of templates: soft templates (micelles, block copolymer aggregates, etc.) and hard templates (silica, polymer nanoparticles, etc.).[7–10] Hollow structures are obtained after removing a template, and preparation is, hence, inherently laborious and time-consuming.

For hollow spheres, mechanical strength and chemical stability are required for many applications. Polyimides (PIs) are a class of representative high-performance polymers with high thermal stability and good mechanical properties.[11] Even though PI nanoparticles and hollow spheres are clearly effective for many applications, such as low dielectric devices, catalyst carriers, and molds, there are only a few reports on the preparation of PI nanoparticles[12–15] and even fewer for porous and hollow PI nanoparticles. These PI hollow spheres are generally fabricated by means of adsorption within polystyrene hollow sphere templates.[16,17] Very recently, Oikawa reported the preparation of nanoporous PI nanoparticles using reprecipitation, with a second polymer (poly(acrylic acid) etc.) as porogen.[18,19] He further fabricated PI spherical nanoparticles with intriguing unique shapes, including doughnut-like and soccer ball-shaped morphologies; unfortunately, the reproducibility of that experimental procedure was poor, and the hollow sphere morphologies are rarely obtained.[20] For most practical applications, a facile, reproducible, and scalable process that allows precise control of the morphologies of the particles is required, as for PI hollow spheres, this kind of method is still not attainable.

In recent years, we have made significant efforts on the preparation of PI nanoparticles with controlled morphologies, for example, we obtained PI nanoparticles with banded morphology and dimple-like morphology through self-assembly.[21,22] Reprecipitation is very simple to perform and has been adapted to the preparation of a wide range of inorganic/organic materials with controllable morphologies.[23,24] Here, we present our preliminary work on the fabrication of PI hollow spheres through fine-tuning the polymer precursor concentration or adding extra salt, obtaining many uniquely shaped objects, including hollow sphere, deflated capsules, bowl-shaped particles, and dimple-like hollow spheres. To the best of our knowledge, such a facile and reproducible process for the fabrication of PI hollow spheres with controllable morphologies has not been reported.

Preparation of hollow spheres is as follows. Poly(amic acid) (PAA), used as a precursor of PI, was synthesized from a spirobisindane-linked dianhydride (SBIDA) and 4,4′-oxydianiline (ODA) in *N*-methyl-2-pyrrolidinone (NMP) solution (Scheme 1). A solution of PAA in NMP (100 μL) with designed concentration was rapidly injected into vigorously stirred cyclohexane (10 mL) using a microsyringe, vigorous stirring was maintained for several minutes. The nanoparticles formed were then chemically imidized through the addition of a mixture of acetic anhydride and triethylamine (1:1, 100 μL) to the dispersion and subsequent stirring overnight, the separated PI nanoparticles were further heating at 270 °C for 1 h to complete the imidization.[29]

An opaque solution was obtained soon after the injection of PAA/NMP solution into cyclohexane. The morphologies of the resulting nanoparticles were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). For the 1 wt% PAA/NMP solution, the SEM image (Figure 1A) clearly reveals a large amount of hollow microspheres with size of several micrometers, most of the time there



Scheme 1. Synthesis of PAA and PI containing SBIDA and ODA.

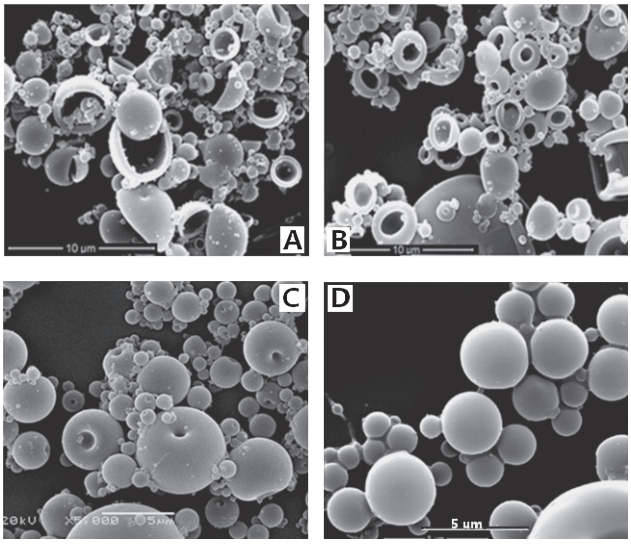


Figure 1. SEM images of PAA hollow spheres with various morphologies by fine-tuning PAA concentrations (A: 1 wt %, bowl-like hollow spheres, B: 2 wt %, deflated hollow spheres, C: 5 wt %, dimple-like hollow spheres, and D: 8 wt %, hollow spheres with complete shell).

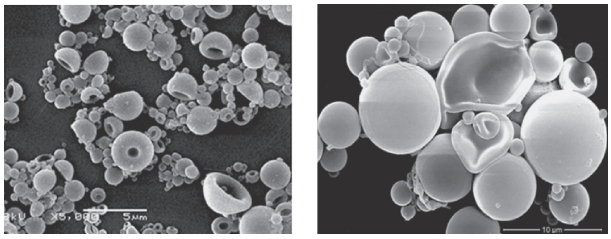


Figure 2. SEM images of PAA hollow spheres with closed shell after adding various LiCl [2 wt % PAA in NMP with 7% (left) and 40% LiCl (right)].

is one big hole in the surface of each microsphere, thus obtaining a bowl-like morphology.

The morphologies of the hollow spheres can be easily controlled by fine-tuning the concentration of PAA solution. As the PAA concentration increases from 1 wt % to 2 wt % to 5 wt % and finally to 8 wt %, the SEM images clearly reveal that the morphologies change from bowl-like (Figure 1A) to deflated sphere (Figure 1B), to dimple-like (Figure 1C), and finally to hollow sphere with complete shells (Figure 1D), thus, revealing a facile control over the morphologies. We found it very interesting that the hollow spheres were obtained with high reproducibility; the mechanism behind this phenomenon is hard to explain. It may relate to the flexible and contorted structures of SBIDA–ODA PI used in our procedure, while for rigid PI with structure similar to commercial PIs like Kapton or Upilex, only solid nanoparticles were observed.

Besides fine-tuning the concentration of PAA solution, we further found that adding salt to the PAA solution has considerable influence on the morphologies of the resulting PI hollow spheres. As shown in Figure 2, after adding 7% or 40% LiCl to the PAA solution, hollow spheres with closed shell were obtained instead of bowl-like morphology with open hole for the 2 wt % PAA solution without salt, no open holes can be

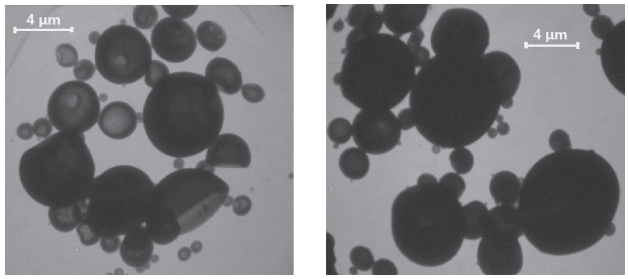
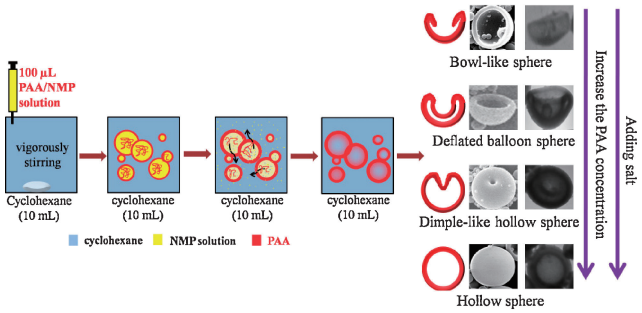


Figure 3. TEM images of PI hollow spheres after imidization [2 wt % PAA in NMP with LiCl 7% (left) and 8 wt % PAA in NMP (right)].



Scheme 2. Mechanism for the formation of hollow PI spheres with various morphologies.

observed. This suggests that the salt helps the formation of continuous polymer shells during phase separation. It is known that the LiCl interacts more strongly with NMP solvent than with the PAA precursors,[20] thus the solvating power of NMP for PAA is progressively reduced with the increase of salt concentration. To some extent, this decrease in solvating power would induce aggregation of the PAA polymer chains and, hence, helps the formation of a robust and continues shell.

The obtained PAA hollow spheres can be further transformed to high-performance PI hollow spheres through imidization, thus fixing the structures. After imidization, the TEM image clearly reveals that the hollow spheres were maintained, with deflated and dimple-like hollow spheres that are similar to those observed before imidization (Figure 3, left). The TEM images further confirmed the existence of hollow spheres; sphere morphologies with darker circles clearly reveal that they all consist of hollow sphere structures (Figure 3).

Such a facile and reproducible process for preparing PI hollow spheres with controllable morphologies is very interesting, and a good understanding of the formation mechanism is required to explore further application of this facile method. Based on the above experimental results, we propose a tentative mechanism to illustrate the formation of hollow spheres with various morphologies (Scheme 2): Initially, after injection, NMP droplets containing PAA precursor immediately form in cyclohexane solution, which is a poor solvent for PAA. Next, reprecipitation of the PAA begins to occur at the interface of droplets, and hollow spheres are formed through the phase inversion of PAA as the NMP molecules gradually diffuse into the cyclohexane solution. For extremely low PAA concentration at 1 wt %, the solid content of PAA is too low to form a continuous shell, most of the hollow spheres are broken, and

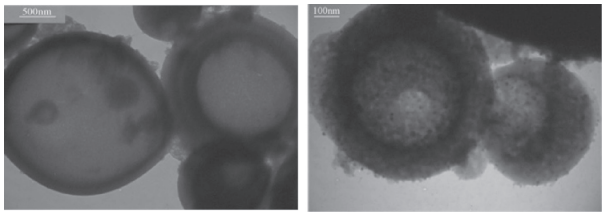


Figure 4. TEM images of PI hollow spheres before (left) and after (right) the growth of Pd nanoparticles.

thus PI hollow spheres with open holes are formed. With increasing PAA concentration to 2 wt %, the PAA content is sufficient to form a complete shell, but it is still not sufficiently robust to maintain its morphology after the evaporation of solvent, thus leading to the deflated spheres. With increasing concentration to 5 wt %, the PAA content is sufficient to form a complete shell with only a small dimple-like morphology, and finally, with PAA content of 8 wt %, PAA solid is robust enough to form hollow spheres with perfect complete shells. With the addition of LiCl, closed PI hollow spheres are obtained even at extremely low PAA concentrations, this may be due to the complex formed between NMP and LiCl, thus enhancing the aggregation of PAA and leading to continuous polymer shells without open holes. However, due to the low solid content, the shells are not strong enough to maintain the morphologies and deflated hollow spheres are observed.

An interesting aspect which may be important for the potential application of these PI hollow spheres is the special rigid and contorted PI main-chain structures derived from 3,3,3′,3′-tetramethyl-1,1′-spirobisindane (Scheme 1). This spiro-center provides a nonlinear shape, and the fused ring structure provides the required rigidity and thus may contain microporous structures in the shell.[25,26] This characteristic facilitates the regulated growth of various metal nanoparticles due to the existence of sub-nanoscale microporous cavities.[27,28] As a proof of concept experiment, the as-prepared hollow spheres were impregnated in a Na_2PdCl_4/methanol solution at ambient temperature. Subsequent reduction of the complexes by a fresh aqueous $NaBH_4$ solution yields stable, relatively monodisperse Pt nanoparticles with a diameter of several nanometers as revealed by TEM (Figure 4). Such robust metal/PI nanocomposite hollow spheres hold promise in molecular catalysis and nanoreactors, and further study is ongoing.

In brief, we have explored a facile and reproducible reprecipitation method for the preparation of high-performance PI hollow spheres, and various novel morphologies, including bowl-like, deflated, dimple-like, and hollow spheres with complete shell, can be easily manufactured by simply changing the PAA concentration. We further found that the added LiCl helps the formation of hollow spheres with closed shell. A mechanism of formation of these various morphologies was proposed based on phase inversion principles. We believe that this facile preparation together with the existence of microporous shells will enable the potential use of these novel materials in fields like supported nanocatalysis, controlled release and ultralow-dielectric-constant films, and further study of the potential broad application of this method is underway.

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References and Notes

1 Y. Zhao, L. Jiang, *Adv. Mater.* **2009**, *21*, 3621.
2 S. H. Joo, J. Y. Park, C.-K. Tsung, Y. Yamada, P. D. Yang, G. A. Somorjai, *Nat. Mater.* **2009**, *8*, 126.
3 S. H. Im, U. Jeong, Y. N. Xia, *Nat. Mater.* **2005**, *4*, 671.
4 D. Kim, E. Kim, J. Lee, S. Hong, W. Sung, N. Lim, C. G. Park, K. Kim, *J. Am. Chem. Soc.* **2010**, *132*, 9908.
5 J. H. Pan, X. Zhang, A. J. Du, D. D. Sun, J. O. Leckie, *J. Am. Chem. Soc.* **2008**, *130*, 11256.
6 X. Liu, M. Jiang, *Angew. Chem., Int. Ed.* **2006**, *45*, 3846.
7 D. Chen, M. Jiang, *Acc. Chem. Res.* **2005**, *38*, 494.
8 Y. Wan, Y. Shi, D. Zhao, *Chem. Mater.* **2008**, *20*, 932.
9 T. L. Kelly, M. O. Wolf, *Chem. Soc. Rev.* **2010**, *39*, 1526.
10 S. M. Marinakos, J. P. Novak, L. C. Brousseau, A. B. House, E. M. Edeki, J. C. Feldhaus, D. L. Feldheim, *J. Am. Chem. Soc.* **1999**, *121*, 8518.
11 *Polyimides*, ed. by D. Wilson, H. D. Stenzenberger, P. M. Hergenrother, Blackie & Son Ltd., Glasgow and London, **1990**.
12 Y. Nagata, Y. Ohnishi, T. Kajiyama, *Polym. J.* **1996**, *28*, 980.
13 Z. Chai, X. Zheng, X. Sun, *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 159.
14 J. Y. Xiong, X. Y. Liu, S. B. Chen, T. S. Chung, *Appl. Phys. Lett.* **2004**, *85*, 5733.
15 M. Suzuki, H. Kasai, T. Ishizaka, H. Miura, S. Okada, H. Oikawa, T. Nihira, H. Fukuro, H. Nakanishi, *J. Nanosci. Nanotechnol.* **2007**, *7*, 2748.
16 S. Watanabe, K. Ueno, K. Kudoh, M. Murata, Y. Masuda, *Macromol. Rapid Commun.* **2000**, *21*, 1323.
17 J. Jing, S. Ding, C. Zhang, C. Chen, X. Rao, G. Dang, Z. Yang, H. Zhou, *Mater. Chem. Phys.* **2009**, *116*, 330.
18 G. Zhao, T. Ishizaka, H. Kasai, H. Oikawa, H. Nakanishi, *Chem. Mater.* **2007**, *19*, 1901.
19 G. Zhao, T. Ishizaka, H. Kasai, M. Hasegawa, H. Nakanishi, H. Oikawa, *Polym. Adv. Technol.* **2009**, *20*, 43.
20 H. Kasai, H. Mitsui, G. Zhao, T. Ishizaka, M. Suzuki, H. Oikawa, H. Nakanishi, *Chem. Lett.* **2008**, *37*, 1056.
21 X. Liu, J. Tang, Y. Zheng, Y. Gu, *J. Polym. Sci., Part B* **2005**, *43*, 1997.
22 X. Liu, J. Liu, M. Jiang, *Macromol. Rapid Commun.* **2009**, *30*, 892.
23 Z. Wang, Z. Li, C. J. Medforth, J. A. Shelnutt, *J. Am. Chem. Soc.* **2007**, *129*, 2440.
24 F. Wang, M.-Y. Han, K. Y. Mya, Y. Wang, Y.-H. Lai, *J. Am. Chem. Soc.* **2005**, *127*, 10350.
25 N. B. McKeown, P. M. Budd, *Chem. Soc. Rev.* **2006**, *35*, 675.
26 B. S. Ghanem, N. B. McKeown, P. M. Budd, J. D. Selbie, D. Fritsch, *Adv. Mater.* **2008**, *20*, 2766.
27 S. N. Sidorov, I. V. Volkov, V. A. Davankov, M. P. Tsyurupa, P. M. Valetsky, L. M. Bronstein, R. Karlinsey, J. W. Zwanziger, V. G. Matveeva, E. M. Sulman, N. V. Lakina, E. A. Wilder, R. J. Spontak, *J. Am. Chem. Soc.* **2001**, *123*, 10502.
28 C. M. Aberg, M. A. Seyam, S. A. Lassell, L. M. Bronstein, R. J. Spontak, *Macromol. Rapid Commun.* **2008**, *29*, 1926.
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