Fabrication of Porous Nanoscale Polyimide Structures

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In the fabrication of polyimide (PI) spherical nanoparticles by the reprecipitation method, intriguing uniquely shaped objects, including doughnut-like and/or hollow, and polymeric soccer ball-shaped PI nanoparticles are rarely obtained. Furthermore, PI fine particles, which possess a hollow core and some 100 nm-sized surface pores leading to the inner hollow, were reproducibly obtained by the improved reprecipitation method.

Hollow and porous spheres in the size from nanometer to micrometer have attracted much interest owing to potential for application in catalysts, chromatographic carriers, adsorbents, low-dielectric fillers, optics, drug storage and delivery carriers. For hollow particles, chemical stability and mechanical strength, and control of permeability, which usually are varied by changing pore size and/or pore number on the surface, are necessary. Recently, a variety of hollow particles with pores on their surfaces, which consist of metals,[1] ceramics,[2–4] polymers,[5–7] have been reported. However, it seems difficult to control the pore size and/or pore number.

Polyimides (PIs) are among the most promising high-performance polymeric materials. Because of their high thermal stability, good mechanical properties, and low dielectric constant, they are widely used in electronics. Although PI nanoparticles are clearly effective for some applications, such as low-dielectric devices, catalyst carriers, filters, and molds, almost all previous studies of PIs and their applications have been performed in the bulk state, including thin films. There are only a few reports on preparing PI fine particles,[8–12] porous PI particles (not hollow),[12–14] and no report on hollow PI fine particles with pores on their surfaces as far as we know.

In recent years, we have fabricated a variety of organic nanocrystals and nanoparticles exhibiting unique optical or chemical properties through the use of a novel reprecipitation method.[15,16] Because this approach is very simple to perform and applicable to a wide range of materials, we became interested in adapting it for the preparation of PI nanoparticles with finely tuned control of size.[11] As part of our ongoing research, we serendipitously obtained a series of interesting nanodesigned porous PI particles. Unfortunately, the reproducibility of that experimental procedure was poor; indeed, we were able to repeat the synthetic procedure only once successfully. Thus, we focused our attention on the reproducible fabrication of porous PI particles through the use of the applied reprecipitation method. Here, we introduce a facile and reproducible fabrication technique for the preparation of porous PI particles possessing a hollow core and report on controlling pore number on the surface. In addition, we suggest mechanisms for formation of porous PI particles.

Poly(amic acid) (PAA), used as a precursor polymer, was synthesized through polyaddition of 4,4′-oxydianiline (ODA) and 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) in *N*-methyl-2-pyrrolidinone (NMP). We investigated the fabrication of PI particles using the following two conditions.

Fabrication conditions A: A solution of PAA (1.54 wt %) in NMP (100 µL) was rapidly injected using a microsyringe into vigorously stirred cyclohexane (10 mL) at 7 °C. It is believed that the doughnut-shaped PAA nanoparticles were produced at this point. The nanoparticles were chemically imidized through the addition of a mixture of pyridine and acetic anhydride (1:1, 100 µL) to the dispersion and subsequent reaction for 2 h. In the following stage, they were converted into doughnut-shaped PI nanoparticles through thermal imidization at 270 °C for 1 h.

Fabrication conditions B: LiCl was added to an NMP solution of PAA [PAA 1.54 wt %, LiCl:PAA 0.05–0.2 (w/w)]. Porous PAA nanoparticles were prepared after injecting this solution into cyclohexane at room temperature, as described above for Conditions A. The nanoparticles were chemically imidized, followed by thermal imidization as described above. Finally, the PI nanoparticles were washed with water to remove any residual LiCl.

When PI nanoparticles are prepared using our reprecipitation method, it is usually possible to control their sizes through changes to various experimental conditions, e.g., the temperature of the poor solvent or the concentration of the injected solution. When the temperature was decreased, the average size of the particles obtained increased.[11] Interestingly, when Conditions A (lower temperature) were employed to prepare particles having sizes greater than 500 nm, we obtained doughnut-like and hollow PI nanoparticles (Figures 1a and 1b). Furthermore, we sometimes produced intriguing uniquely shaped objects under otherwise identical conditions. For example, Figure 1c displays 300-nm-diameter polymeric soccer ball-shaped particles that exhibit both pentagonal and hexagonal facets. The line widths of the facet frames, which are composed of polymer, were ca. 50 nm. We are unaware of any such organic and/or polymeric nanomaterials having been reported previously.

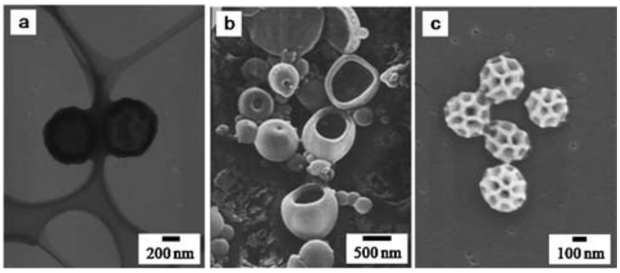

Figure 1. a) TEM and b), c) SEM images of PI nanoparticles fabricated using Conditions A.

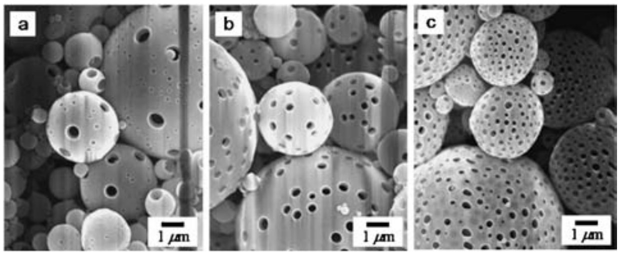

Figure 2. SEM images of porous PI particles fabricated using Conditions B. Content of LiCl (relative to PAA) in the NMP solution: a) 5, b) 10, and c) 20 wt %.

Unfortunately, further research will be necessary to improve the reproducibility of our results; indeed, we successfully obtained soccer ball-shaped particles such as those in Figure 1c less than 5% of the time. Nevertheless, we believe that the ability to prepare these new types of nanosized polymer particles should be of interest to many researchers in this field.

In our present study, we fine-tuned the reprecipitation method to improve the reproducibility of forming porous PI nanostructured materials by using Conditions B. Figure 2 displays SEM images of the porous PI particles obtained after imidization and removal of the salt through washing with water. Size distribution of the particles was too large as shown in this SEM images. In previous study, the same result was obtained, i.e., when mean size of particles obtained was large (several μm), their size distribution was large.[11] Increasing the weight ratio of LiCl to PAA in the injected solution led to an increase in the number of holes in the porous particles. The diameters of the holes on the surfaces of the particles were almost all ca. 100 nm. Figure 3 presents TEM images of the porous PI particles. We observed that spherical holes existed within the particles, which could be divided roughly into two types of porous materials. When the particle size was 700 nm or above, we observed hollow particles, each having a single huge hole in their center; for particle sizes below 700 nm, we observed a number of holes of almost equal size within the particles.

We found that porous particles were already fabricated before chemical imidization (see Supporting Information[19]). We believe that the mechanism for generating these porous particles occurs as follows: Initially, NMP droplets containing PAA and LiCl were generated in the poor solvent immediately after injection. Next, reprecipitation of the PAA began as the NMP molecules gradually dissolved in the cyclohexane. At this stage, porous particles featuring some holes were formed in the droplets through phase separation of the polymer units. At the same time, LiCl and NMP species became concentrated within the holes because LiCl–NMP interactions are stronger than PAA–NMP interactions.[17,18] Finally, NMP and LiCl eluted perfectly from the polymer system and into the cyclohexane. Indeed, we did not detect any LiCl in the final products. The porous PI particles were then obtained through subsequent imidization, the extent of which we estimated from IR spectroscopic data to be above 90%.

In conclusion, we have serendipitously obtained a new type of PI nanoparticle, shaped like a soccer ball, through the use of a reprecipitation method. Through improvements to this method, we were able to reproduce the fabrication of these particles successfully. Furthermore, we proposed the mechanism of formation of these uniquely shaped PI particles. Above all, we hope that the existence of nanometer-sized soccer ball-shaped polymeric particles will encourage others in the field of polymer science to investigate the properties and uses of these novel materials.

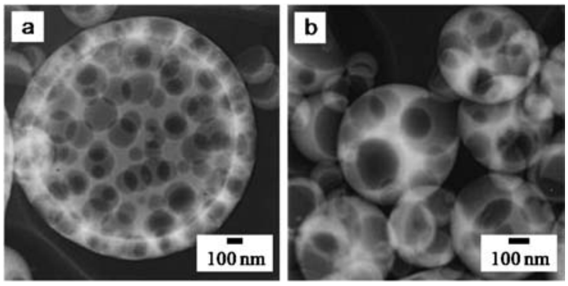

Figure 3. TEM images of the porous PI particles fabricated using Conditions B. a) Large (>700 nm) hollow-type porous particles containing a single huge hole; b) small (<700 nm) porous particles containing multiple, equally sized holes.

We are grateful for the support for this research provided by a grant from the CREST (Core Research for Evolution Science and Technology) program of the Japan Science and Technology Corporation (JST).

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19 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.