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Synthesis of Hollow Asymmetrical Silica Dumbbells with a Movable Inner Core

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Hollow asymmetrical silica dumbbells containing a movable inner core were fabricated by a template-assisted method. Three different templates were employed for the fabrication of the hollow asymmetrical dumbbells. For the preparation of the first template, silica particles were uniformly covered with a cross-linked polymethylmethacrylate (PMMA) shell and the polymerization of styrene was conducted to induce a protrusion of polystyrene (PSt) from the PMMA shell. Anisotropic colloids composed of silica, PMMA, and PSt were used as templates, coated with a silica shell, and held at 500 °C for 2 h to remove the polymer interior components of the template colloid. The heat treatment successfully produced hollow asymmetrical silica dumbbells containing an inner silica core. After being dried, approximately 50% of the inner silica particles that were originally coated with PMMA ended up in the other hollow sphere in which the PSt component existed before heat treatment, indicating that the inner silica particles could pass through the hollow asymmetrical dumbbells' necks and were free to move in the interior. In the preparation of the second and third asymmetrical dumbbell templates, magnetic silica particles and titania particles, respectively, were covered with a PMMA shell to incorporate externally responsive particles into the hollow silica shells as above. The successful syntheses demonstrated the generality of our approach. The passage of the responsive particles through the dumbbell's neck enabled active control of the position of the responsive particles inside the asymmetrical dumbbells by external fields.

1. Introduction

Hollow nanomaterials have attracted a great deal of attention because of their potential in many fields, including their use as drug carriers,[1,2] reaction vessels,[3,4] and building blocks of photonic crystals.[5] A variety of chemical and physicochemical methods have been developed for the production of hollow nanomaterials.[6−14] (For a recent review, see ref 15). Template-assisted methods are commonly used to synthesize hollow nanomaterials of various sizes and shapes. In most template-assisted methods, colloidal templates have been coated with different materials by sol−gel processes,[16] the layer-by-layer approach,[17] or chemical deposition.[18] Removal of the colloidal template by chemical dissolution or thermal calcination can produce the corresponding hollow particles.

The application of nonspherical particles to the template-assisted method enables the creation of hollow particles with various unique structures. For instance, hollow silica ellipsoids were successfully prepared by silica coating hematite spindles and dissolving the hematite in hydrochloric acid.[19] Hollow SnO_2 ellipsoids with a movable hematite core could be created from a template of hematite spindles coated with SiO_2 and SnO_2, respectively.[20] The doubly coated spindles were immersed in NaOH solution to dissolve the middle layer of silica. Similar hollow architectures that contain a movable spindle have been fabricated from a template of hematite spindles coated with an inner silica shell and an outer polymer shell.[16]

Here, we present hollow particles composed of a uniquely tunable shaped outer shell and a movable inner sphere. The outer shell is composed of two silica spheres of different sizes. The synthesis route to the architecture in the present work is shown in Figure 1. The procedure consists of four steps: (1) coating core particles with cross-linked polymethylmethacrylate (PMMA), (2) the creation of a protrusion of polystyrene (PSt) on the polymer-coated particles, (3) silica coating, and (4) the removal of the polymer components with heat treatment. After thermal decomposition of the polymer components in the silica shell, hollow

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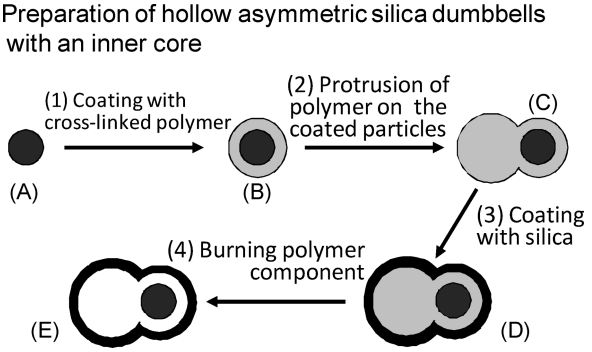

Figure 1. Schematic procedure for the preparation of hollow asymmetrical silica dumbbells with an inner core.

asymmetrical silica dumbbells with a movable inner core will be obtained. Some of the authors previously succeeded in the preparation of asymmetrical polymer dumbbells (snowman-shaped polymer particles) containing a silica core with soap-free emulsion polymerization in the presence of a reactive silane coupling agent.[21] In this report, we first use such silica-core-based composite asymmetrical dumbbells as a template to demonstrate the synthesis route shown in Figure 1. Next, other dumbbell templates that have the same polymer components but a different inner sphere were also employed for the preparation of hollow asymmetrical dumbbells that are responsive to external fields and indicate the generality of our approach. When externally responsive cores are incorporated into the hollow asymmetrical dumbbells with an inner neck wider than the size of the responsive core, one expects that the position of the inner core can be moved from one end of the particle to the other by an external field. Thus, in this report, two different responsive cores of magnetic silica particles (consisting of silica and Fe_3O_4/γ-Fe_2O_3) and titania particles were respectively incorporated into the hollow asymmetrical dumbbells instead of the pure silica particles.

2. Experimental Section

Chemicals. Methyl methacrylate (MMA, 98%), styrene (St, 99%), sodium *p*-styrenesulfonate (NaSS), potassium persulfate (KPS, 95%), teraethyl orthosilicate (TEOS, 95%), ethanol (99.5%), ammonia aqueous solution (25 wt %), and polyvinylpyrrolidone (PVP, K-90, M_w = 360 000 g/mol) were obtained from Wako Pure Chemical Industries (Osaka, Japan). The inhibitor of MMA was removed by an inhibitor removal column, and St was washed with a 0.1 M sodium hydroxide solution. The other chemicals were used as received. Silane coupling agent 3-methacryloxypropyltrimethoxysilane (MPTMS, 95%) and cationic polymer poly(allylamine hydrochloride) (PAH, M_w = 15 000 g/mol) were purchased from Shinetsu Chemical (Tokyo, Japan) and Sigma-Aldrich Corporation, respectively, and used as received.

Synthesis of Asymmetrical Dumbbells without a Core. Hollow asymmetrical silica dumbbells without any cores were prepared with a combination of double polymerization, silica coating, and pyrolysis of the polymer components. First, deionized water (78.7 g) was bubbled with nitrogen for 30 min, and 96 μL of MPTMS was added to the water. After an hour, 5.29 mL of MMA was added to the mixture. After 30 min, the mixed solution was heated to 65 °C and 10 mL of an aqueous solution containing 0.108 g of KPS was added to the mixed solution. After 10 min, 5 mL of an aqueous solution of 0.021 g of NaSS was added to the reactant solution. The solution was stirred for 2 h at a constant temperature (65 °C). Second, a 5 mL suspension of the PMMA particles obtained after a centrifugation step was added to 83.9 mL of deionized water. The solution was bubbled with nitrogen for 30 min, followed by the addition of 2.3 mL of St. After 2 h, the mixture was heated to 65 °C and an aqueous solution of 0.081 g of KPS was added to the mixture. The polymerization of St was conducted at a PMMA particle concentration of 0.25 vol %. Third, the asymmetrical polymer dumbbells were coated with silica.[22,23] A 2 mL suspension of the PMMA-PSt particles (1.2 vol %) was added to a 5 mL solution containing PAH (1 g/L) and NaCl (0.05 mol/L). The concentration of the asymmetrical polymer dumbbells in the mixture was 0.34 vol %. After two centrifugation steps, the particles were redispersed into a 7 mL ethanolic solution containing 49 mg of PVP. Two more centrifugation steps were used to remove excess PVP, and the particles were redispersed into 10 mL of ethanol. To the ethanolic solution were added a 0.8 mL ammonia solution and 100 μL of TEOS. Finally, the PMMA-PSt polymer particles coated with silica were dried, followed by heat treatment for 2 h in air in a 500 °C oven.

Synthesis of Asymmetrical Dumbbells with a Silica Core. Hollow asymmetrical silica dumbbells containing a silica core were prepared according to the synthesis procedure shown in Figure 1. First, deionized water (16.4 g) was bubbled with nitrogen for 30 min, and 19 μL of MPTMS and 1.6 mL of an aqueous suspension of silica particles at 120 g/L were added to the water. The silica particles (d_V = 310 nm) were prepared using the Stöber method at [TEOS] = 0.2 M, [H_2O] = 5.0 M, and [NH_3] = 1.0 M in ethanol. After 30 min of stirring, 0.851 mL of MMA and 10 mL of an aqueous solution containing 0.0083 g of NaSS were added to the aqueous solution of MPTMS and silica. After 2 h, the mixed solution was heated to 65 °C and 10 mL of an aqueous solution containing 0.0216 g of KPS was added to the mixed solution. The solution was stirred for 3 h at constant temperature (65 °C). Then, a 4.1 mL suspension of the coated particles obtained after three centrifugation steps and redispersion in pure water was added to 20 mL of deionized water (0.12 vol % PMMA-coated silica particle concentration). This solution was bubbled with nitrogen for 30 min, followed by the addition of 0.921 mL of St. After 4 h of waiting, the mixture was heated to 65 °C and 10 mL of an aqueous solution containing 0.0216 g of KPS was added. Third, the asymmetrical polymer dumbbells were silica coated via the method employed for the PMMA-PSt particles above and heated for 2 h in air in a 500 °C oven.

Synthesis of Asymmetrical Dumbbells with a Functional Core. The magnetic silica particles incorporated into the hollow asymmetrical dumbbells were synthesized according to the previous report.[24] In the synthesis procedure, monodisperse silica particles were treated with two cycles of coatings that consist of the heterocoagulation of silica particles with positively charged magnetic nanoparticles (Fe_3O_4/γ-Fe_2O_3) and the precipitation of silica in a sodium silicate solution. The two cycles of coatings produced highly monodisperse magnetic silica particles with multilayers of silica core/magnetic nanoparticles/silica/magnetic nanoparticles/silica. The multilayered particles were further coated with another silica shell by the hydrolysis and condensation of TEOS to improve the colloidal stability of the magnetic silica particles. The multilayered particles were used as inner cores in the MMA polymerization.

Titania particles incorporated into the hollow asymmetrical dumbbells were prepared via hydrolysis and condensation of titanium tetraisoproxide in a mixed solvent of ethanol and acetonitrile.[25] The amorphous titania particles were directly coated with PMMA by the method employed to coat the silica particles and the magnetic silica particles.

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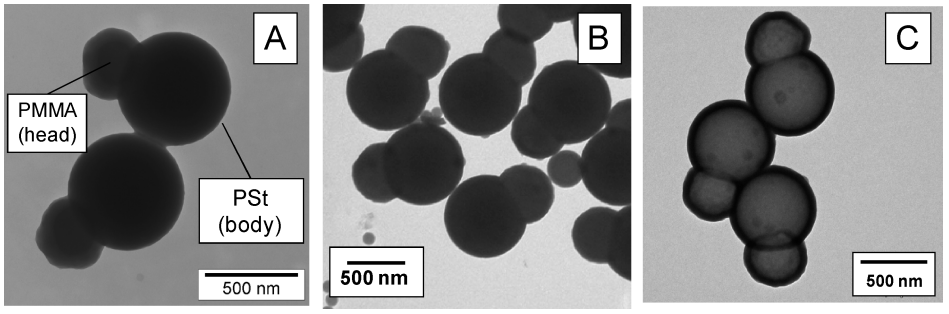

Figure 2. TEM images of asymmetrical dumbbells (A), asymmetrical dumbbells coated with silica (B), and hollow asymmetrical silica dumbbells (C) obtained after heating the particle (B).

Characterization. Asymmetrical silica dumbbells without silica particles were observed with TEM (FEI, Technai F20), and asymmetrical silica dumbbells with silica and functinal cores were observed with TEM (Carl Zeiss, LEO912AB) and FE-TEM (Hitachi, HF-2000). X-ray diffractiometry (XRD) was applied to the characterization of the titania particles coated with a PMMA shell. The magnetization of the magnetic particles was measured with vibrating sample magnetometry (VSM) at ambient temperature. Energy dispersive X-ray spectroscopy (EDX) for hollow asymmetrical dumbbells incorporating magnetic silica particles was performed by STEM (Hitachi, HD-2700B) equipped with a Noran System Six EDX.

3. Results and Discussion

Synthesis of Asymmetrical Dumbbells without a Core. Prior to the fabrication of hollow asymmetrical dumbbells with an inner core (Figure 1E), hollow asymmetrical dumbbells without any inner core were prepared to examine and optimize the thickness of the outer silica shell that is necessary to maintain the unique shape.[22,26,27] In the preparation, pure asymmetrical polymer dumbbells shown in Figure 2A were used as a template. In the following text, the asymmetrical dumbbells that we made will be described as "snowman" particles with the smaller sphere of PMMA forming the head and the larger sphere of PSt forming the body. The TEM image shows that the snowman particles were approximately 850 nm tall, 390 nm wide for the head, and 620 nm wide for the body. Another characteristic feature of the snowman particles is their surface morphology. The surface of the PMMA heads was slightly rougher than that of the PSt body, which was probably caused by the cross-linking of PMMA with the silane coupling agent used in the first step of MMA polymerization.[21,28]

The asymmetrical dumbbells were coated with silica shells according to a method previously reported.[22,23] Figure 2B shows a TEM image of the asymmetrical dumbbells obtained after being silica coated. The TEM image shows that the shapes of the particles in Figure 2B were similar to those of the particles in Figure 2A although a small number of secondary particles were generated that could be easily removed by repeated centrifugation. The silica-coated particles were dried and kept at 500 °C in air for 2 h in a furnace to obtain hollow particles with the corresponding shape. Figure 2C shows a TEM image of the empty silica shell with an asymmetrical dumbbell shape after the thermal decomposition of the polymer. The TEM image indicates that the polymer components inside the silica shells were successfully burnt away after the heat treatment. The thickness of the silica shell in Figure 2C is approximately 60 nm, which is clearly thick enough to maintain the original template particle shape and is in line with previous work by some of us in which it was shown that a minimal silica thickness is necessary for this to occur.[26,27]

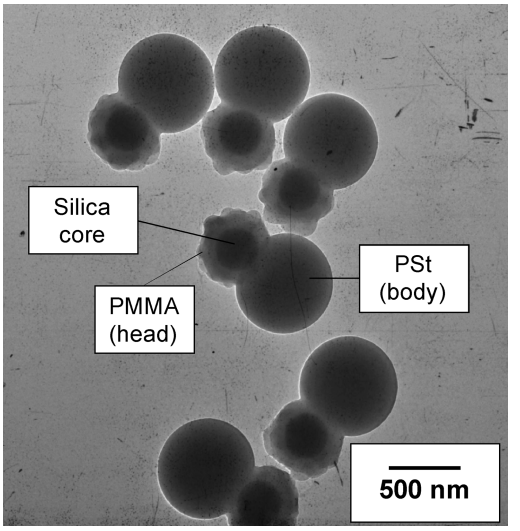

Figure 3. TEM image of asymmetrical dumbbells composed of PMMA-coated silica (head) and PSt (body).

Synthesis of Asymmetrical Dumbbells with a Silica Core. To obtain hollow asymmetrical silica dumbbells with an inner core, silica particles were coated with cross-linked PMMA, and the polymerization of St was conducted in the presence of the PMMA-coated silica particles, as shown in Figure 1. Figure 3 shows a TEM image of asymmetrical composite dumbbells as illustrated schematically in Figure 1C. The asymmetrical dumbbells were composed of a PMMA-coated silica head and a PSt body. They were approximately 1050 nm tall, 560 nm wide for the head, and 710 nm wide for the body (slightly larger than the particles without cores shown in Figure 2A). The TEM analysis indicated that the snowman particles were quite monodisperse with a polydispersity in the length of about 3%. Again, the surface of the PMMA head is rougher than that of the PSt body, similar to the TEM image in Figure 2A.

In the fabrication of the hollow asymmetrical silica dumbbells with a movable inner core, the size of the dumbbell inner neck is important if the inner core has to pass through the neck. The neck size of the asymmetrical dumbbells in Figure 3 was roughly 400 nm and thus larger than the average size of the silica cores (d_{V_silica} = 310 nm). Subsequently, the asymmetrical composite dumbbells were silica coated as before and were held at 500 °C for 2 h. Figure 4 shows a TEM image of the hollow particles obtained after the heating step. The TEM image demonstrates that a silica core was introduced into each hollow asymmetrical dumbbell. (See Supporting Information Figure S-1 for an overview). Upon closer

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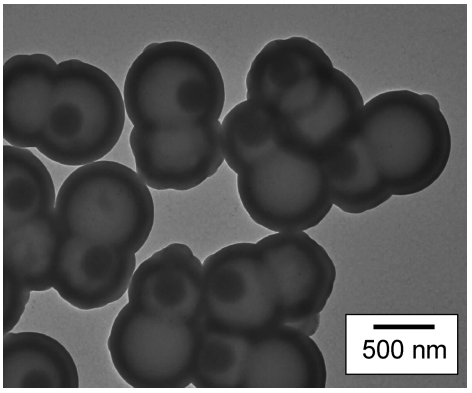

Figure 4. FE-TEM image of hollow asymmetrical silica dumbbells obtained after the silica coating and heating of the particles in Figure 3.

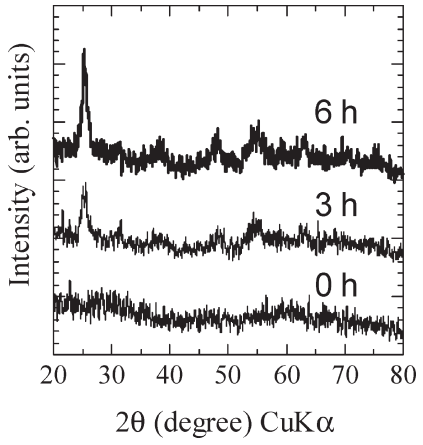

Figure 5. XRD patterns of PMMA-coated titania particles held at 600 °C for 0, 3, and 6 h.

examination of 50 asymmetrical dumbbells, 55% of the silica cores were found in the head and 45% were found in the body. This distribution indicates that, at least during the heating step or the drying in TEM sample preparation, the silica cores were distributed throughout the silica shell and thus could move past the asymmetrical dumbbell's neck.

Synthesis of Asymmetrical Dumbbells with a Functional Core. The hollow asymmetrical dumbbells were functionalized by incorporating titania particles that are expected to be highly responsive to electric fields, both of low and high (optical) frequency. Monodisperse, amorphous titania particles ($d_{V\_titania}$ = 270 nm) that we previously reported[25] were selected for the incorporation because the amorphous titania particles can be crystallized in the heating process used for the thermal decomposition of the polymer components. Prior to incorporation, the crystallization temperature was examined with titania particles were coated with PMMA. The polymer-coated titania particles were heated in air under various conditions. XRD patterns in Figure 5 show that the polymer-coated tiania particles can be crystallized to anatase at 600 °C for 3 h. This heat treatment was applied to the silica-coated dumbbells incorporating amorphous titania particles, which produced the asymmetrical dumbbells shown in the TEM image in Figure 6A. The Figure indicates that the size of the titania particles was shrunk to approximately 250 nm during the heat treatment, which allowed some of titania cores to move from the snowman head to the body.

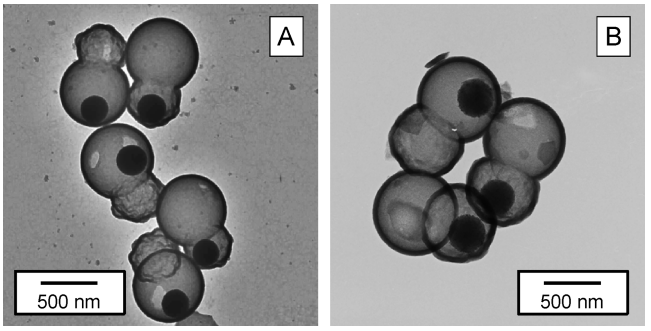

Figure 6. FE-TEM images of hollow asymmetrical dumbbells incorporating a titania core (A) and a magnetic core (B).

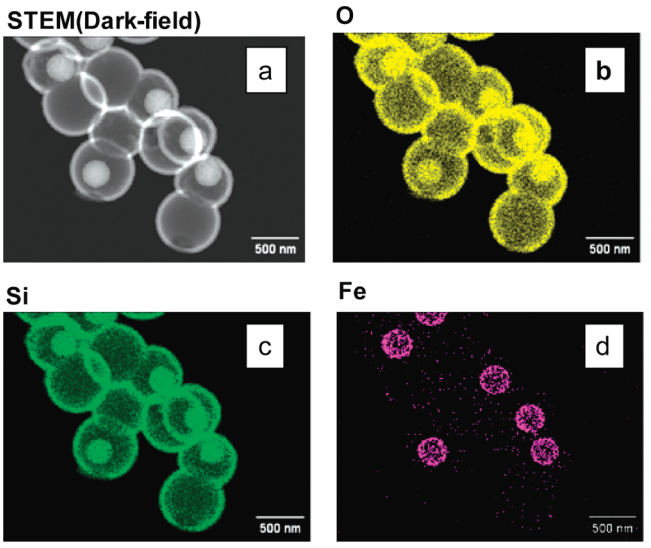

Figure 7. STEM image (dark field, a) and elemental mapping images of the hollow asymmetrical silica dumbbells in Figure 6B. The mapping images in panels b−d indicate oxygen (b), silicon (c), and iron (d), respectively.

To functionalize the hollow asymmetrical silica dumbbells even further with magnetism, magnetic silica particles that some of us recently reported[24] were introduced into the hollow asymmetrical dumbbells. The magnetic silica particles have an average diameter of 320 nm, a coefficient of variation (CV) of 3.5%, and a saturation magnetization of 4.0 emu/g. Figure 6B shows a TEM image of the hollow asymmetrical silica dumbbells with the magnetic silica particles incorporated. Again, the TEM image indicated that incorporation was 100% and that the average diameter of inner magnetic particles in the silica shell was 310 nm, which is slightly smaller than the inner neck size (~360 nm) of the hollow asymmetrical dumbbells. The slight decrease in the inner particle size with heat treatment helped the particles to pass through the inner neck. The 100% incorporation could also be confirmed by the STEM image shown in Figure 7. The spheres in Figure 7 were clearly separated by a uniform shell of the hollow asymmetrical dumbbells. The elemental mapping in Figure 7b,c verified that the shell of the dumbbells was composed of Si and O and that the core consisted of Si, O, and Fe. The saturation magnetization of the hollow dumbbells, measured after heating (N_2 atmosphere, 500 °C, 4 h), was 1.1 emu/g. Magnetic cores are not interesting only because they can be moved or switched between the two compartments within the dumbbell with a magnetic field but also because they can be heated efficiently

with alternating magnetic fields,[29] which could possibly be used to break the shell.

The particle sizes reported in this article make direct imaging of the movements inside the particles difficult. However, it is clear that the effects on particle scattering are still significant but this measurement is outside the scope of the present article. For instance, 2D or 3D colloidal crystals made from our particles would have the interesting property that the application of an electric field (or a magnetic field for the magnetic spheres) could switch all of the particles to such positions that the form factors of all of the particles would become identical and thus would support Bragg scattering. However, if the scattering cores would more randomly distribute themselves on the lattice by Brownian motion, then a Bragg peak would be absent or strongly reduced in height. Moreover, dumbbells responsive to an external field can be use to form interesting conformations such as chiral strings,[30] indicating that our particles are also interesting from the standpoint of realizing 1D structures as well. Work is currently in progress to increase particle sizes to observe the field-induced movement of inner cores directly with a microscope and further characterize the tunable scattering properties as well.

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4. Conclusion

Hollow asymmetrical silica dumbbells with a movable silica core were fabricated with a template-assisted method. By changing the sizes of the spheres or compartments that make up the dumbbells, there is freedom in the anisotropy of the design of the shells. Functional core incorporation into the asymmetrical dumbbells was demonstrated for both magnetic silica particles and high-index titania particles. Extension to other interesting functional core particles such as metallic or semiconductor nanoparticles is straightforward because methods exist to coat such particles with a silica shell. The ability to address the movable cores with external fields not only will allow control over the particle properties by techniques such as heating (e.g., by light or magnetic fields) but also will allow for coherent modulation or switching of the scattering properties, which is quite interesting in many photonic applications.

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Supporting Information Available: FE-TEM images to indicate an overall view of the hollow asymmetrical silica dumbbells with a silica core. This material is available free of charge via the Internet at http://pubs.acs.org.