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Synthesis of Hollow Metal Oxide Nanospheres by Templating Polymeric Micelles with Core−Shell−Corona Architecture

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Hollow metal oxide nanospheres, such as niobium pentoxide, cerium oxide, and vanadia, have been successfully synthesized, for the first time, by templating a polymeric micelle of poly(styrene-*b*-2-vinyl-1-methylpyridinium iodide-*b*-ethylene oxide) (PS−PVMP−PEO). PS−PVMP−PEO forms a micelle with a PS core, a PVMP shell, and a PEO corona in aqueous solutions. The significance of the present method is that each block of the copolymer has its unique function in the synthesis of hollow metal oxide nanospheres; the PS core plays the role of a template of the cavity, while the cationic PVMP shell works as a reservoir and nanoreactor for the precursors of the metal oxides and the PEO corona stabilizes the polymer/inorganic hybrid to prevent secondary aggregate formation.

Metal oxides have many applications because their special electrical, optical, and magnetic performances. They have been used as ceramic and semiconductor materials in various fields. For instance, niobium pentoxide (Nb_2O_5) is used in the production of capacitors and optical glasses as well as a support of metal oxide catalysts.[1,2] Thus, many groups have proposed a variety of methods to synthesize metal oxide nanoparticles.[3−10] Among the metal oxide nanoparticles, however, only a small number of studies have been devoted to *hollow* nanospheres, because they are relatively new materials compared to conventional *dense* nanospheres. Especially, there have never been studies on the hollow nanospheres of Nb_2O_5, CeO_2, and V_2O_5, although these hollow nanospheres have potential applications in many fields based on their characteristics of low density, large surface area, and surface permeability. Therefore, we tried to synthesize the hollow nanospheres of Nb_2O_5, CeO_2, and V_2O_5 in this study.

We have recently succeeded in the synthesis of hollow silica nanospheres using a template of polymeric micelles with a core−shell−corona structure.[11] The micelle of poly(styrene-*b*-2-vinylpyridine-*b*-ethylene oxide) (PS−PVP−PEO), consisting of a PS core, a PVP shell, and a PEO corona, was used as the template because the micelle of this polymer has been well characterized by several groups.[12,13] In this method, the PS core acts as a template of the cavity, the PVP shell plays the role of a reservoir and reactor for the silica precursor, and the PEO corona helps in the stabilization of the polymer/silica hybrid particles to prevent the formation of secondary aggregates. Silica was deposited in the PVP shell domain by the sol−gel reaction of tetramethoxysilane.[11,14] The polymer/silica hybrid particles were then calcined to remove the polymer template, thus leaving the hollow silica nanospheres. The features of this method are that the core, shell, and corona of the template micelle have their own specific functions to form a well-defined shape, controlled size of the cavity and silica wall, and less aggregated powders with a good dispersibility in water.

In spite of these unique features, however, the previous method has a drawback that the PVP block is not ionized at a pH higher than 5, so that the PVP block cannot work as a reservoir and nanoreactor for the precursor under neutral and basic conditions. Therefore, the reaction is limited to acidic conditions. This is a serious problem for the synthesis of

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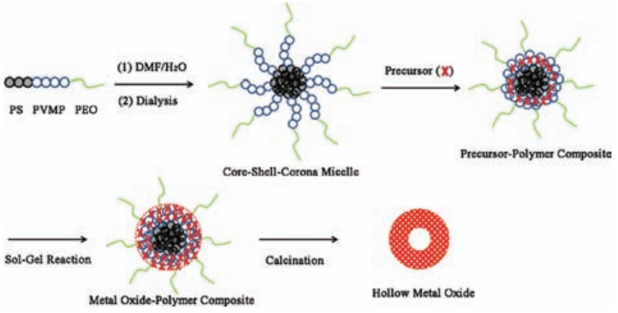
Scheme 1. Fabrication of Hollow Metal Oxide Nanospheres from a PS−PVMP−PEO Micelle Template



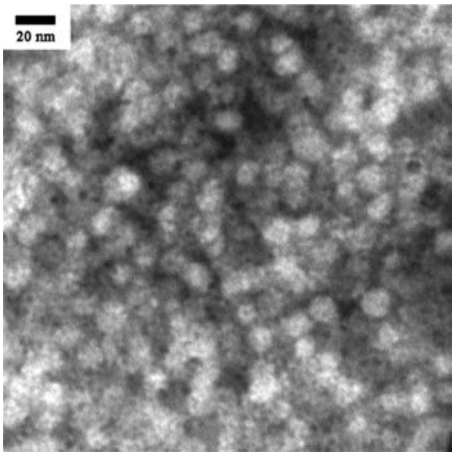


Figure 1. TEM picture of the PS−PVMP−PEO micelle. The TEM sample was prepared from an aqueous solution at a polymer concentration of 1 g/L. The micelle was stained with phosphotungstic acid.

some metal oxides. To solve this problem, we tried to quaternize the PVP block. Once the PVP block is quaternized, the cationic shell can be obtained over a wider pH ranging from acidic to basic conditions and work as a reservoir and nanoreactor for the metal oxide precursors. By using this technique, we have succeeded in fabricating the hollow nanospheres of Nb_2O_5, CeO_2, and V_2O_5. The procedure of the new technique is shown in Scheme 1.

The PS (45K)−PVP (16K)−PEO (8.5K) triblock copolymer was obtained from Polymer Source. The numbers in parentheses are the molecular weights of the corresponding block chains. The PVP block is quaternized by iodomethane in a tetrahydrofuran/methanol (1:1, v/v) mixture at 60 °C. The product, poly(styrene-*b*-2-vinyl-1-methylpyridinium iodide-*b*-ethylene oxide) (abbreviated as PS−PVMP−PEO), was precipitated in hexane. The degree of quarternization is about 100%, as confirmed by NMR (Figure S1 in Supporting Information). Details of the characterization of PS−PVMP−PEO are reported elsewhere.[15]

To prepare the template polymeric micelle, PS−PVMP−PEO was dissolved in *N*,*N*-dimethylformamide at an initial concentration of 1 wt %. After it was completely dissolved, water was added dropwise to the solution with vigorous stirring until the water content reached 15 wt %. The rate of water addition was 1 wt %/min. More water was added to the solution to make a final polymer concentration of 0.5 wt %. The solution was then dialyzed against water to obtain the micelle solution.

The hydrodynamic diameter of the PS−PVMP−PEO micelle was measured by dynamic light scattering and found to be around 150 nm. The micelle morphology was examined by transmission electron microscopy (TEM) using a JEOL JEM-1210 microscope at a voltage of 80 kV, after the micelle sample was stained with phosphotungstic acid. The obtained TEM picture is shown in Figure 1. The white spheres correspond to the hard PS cores of the micelles. It is clear from the TEM picture that the micelle has a spherical structure.

To prepare the hollow nanoparticles of Nb_2O_5, CeO_2, and V_2O_5, niobium(V) ethoxide, cerium sulfate, and ammonium vanadate(V) were employed as the precursors, respectively. According to the literature,[16−19] the isoelectric points of these metal oxides are around pH 4, 7, and 3, respectively, for Nb_2O_5, CeO_2, and V_2O_5. A specific amount [niobium(V) ethoxide, 26.5 mg; cerium sulfate, 39 mg; ammonium vanadate(V), 2 mg] of each precursor was added to 5 mL of the micelle solution by agitating with a magnetic stirrer. A NaOH solution was used to adjust the pH if necessary. The solution was stirred for 1 or 2 days and stored for 2 days without stirring to obtain the polymer/metal oxide hybrid. The polymer/metal oxide hybrid was separated from the solution by centrifugation and dried in an oven at 50 °C. To obtain hollow particles, the polymer template was removed by calcination at 500 °C for 4 h. The removal of the template polymer was confirmed by Fourier transform infrared (FTIR) measurements. It is clear from the FTIR spectra (Figure S2 in Supporting Information) that the C=C vibrational band of the phenyl group (around 1500 cm^{-1}) and the CH_2 vibrational band of the polymer main chain (around 2800 cm^{-1}) are completely lost after calcination. To prepare the samples of the TEM measurements, the products were dispersed in water, followed by casting on a copper grid. The TEM pictures were taken by a JEOL-2000FX microscope at a voltage of 200 kV.

Figure 2a illustrates the hollow Nb_2O_5 nanospheres. Almost all of the particles have a spherical hollow structure with a similar wall thickness. The diameter of the cavity is approximately 12 nm, while the wall thickness is approximately 6 nm. The molar ratio of the 1-methylpyridinium (MP) group in the PVMP block to the precursor is 1:10. Different concentrations of the precursor were also investigated (1:5 and 1:15; Figures S3 and S4 in Supporting Information). When the molar ratio of MP to the precursor was 1:5, no hollow nanospheres were obtained. On the other hand, a network structure was obtained when the 1:15 molar ratio was used. This fact indicates that a critical concentration of the precursor is necessary to prepare the hollow Nb_2O_5.

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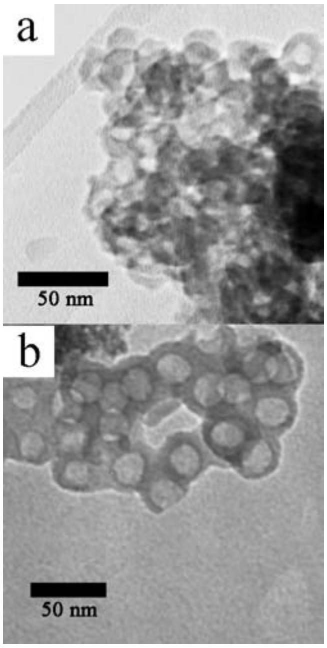

Figure 2. TEM pictures of (a) hollow Nb_2O_5 and (b) hollow CeO_2 nanospheres prepared by templating the PS−PVMP−PEO micelle. The concentration of PS−PVMP−PEO is 1 g/L, and the molar ratio of MP to the precursor is 1:10 in both samples.

Figure 2b is a TEM image of the hollow CeO_2 nanospheres. As is clearly seen in the TEM image, uniform hollow spheres are obtained. The inner diameter is approximately 17 nm, and the wall thickness is approximately 9 nm.

It is interesting to compare the cavity size of the Nb_2O_5 and CeO_2 nanospheres because the same template micelle was used for their syntheses. Because the PS core acts as the template of the cavity for the hollow nanospheres, the cavity diameters should be the same in both particles. However, the obtained cavity diameter is approximately 12 nm in Nb_2O_5, whereas it is approximately 17 nm in CeO_2. This difference seems to be attributed to "shrinking" during calcination. It has been reported by several groups[11,20,21] that the cavity size of the hollow inorganic particles becomes smaller than the size of the template polymers, which is ascribed to the shrinking of the particles during the calcinations. Therefore, it seems that the Nb_2O_5 and CeO_2 walls shrank to different degrees.

We also obtained hollow nanospheres of V_2O_5 (Figure S5 in Supporting Information). The TEM picture shows a clear hollow structure of V_2O_5. However, we sometimes met considerable aggregation in the synthesis of V_2O_5 hollow nanospheres. This might be attributed to the fast hydrolysis of the V_2O_5 precursor in the aqueous micellar solutions. Once the precursor was added to the micellar solutions, precipitation of the product immediately occurred, indicating that the sol−gel reaction started in the aqueous bulk phase before the precursor was incorporated into the template micelles. This might result in nontemplated structures of aggregated products. Thus, the rate of hydrolysis of the precursors seems to be one of the key factors in obtaining well-controlled hollow nanospheres. We have to determine the conditions under which hydrolysis of the precursor of V_2O_5 is retarded. This will be extensively investigated in future studies.

In summary, we have succeeded in the fabrication of hollow nanospheres of Nb_2O_5, CeO_2, and V_2O_5 by templating the polymeric micelle of PS−PVMP−PEO, which has a PS core, a PVMP shell, and a PEO corona in aqueous solutions. All of the obtained metal oxide nanoparticles have a spherical shape with a uniform cavity size and wall thickness. It was found that the rate of hydrolysis of the precursors is one of the key factors in obtaining nanospheres with a well-controlled structure. To the best of our knowledge, this is the first paper that reports the synthesis of hollow nanospheres of Nb_2O_5, CeO_2, and V_2O_5.

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Supporting Information Available: NMR spectra of the polymer before and after quaternization, FTIR spectra of the hybrid before and after calcination, and TEM images of niobium oxide particles and hollow vanadia nanospheres. This material is available free of charge via the Internet at http://pubs.acs.org.

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