

Template Synthesis of Monodisperse Mesoporous Titania Spheres

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Mesoporous titania spheres with a high monodispersity were synthesized by employing monodisperse poly(styrene-*co*-methacrylic acid) (PSMAA) particles as templates. The titania nanoparticles coated on the PSMAA spheres were first redispersed in the mixed solvent and subsequently infiltrated into the swollen PSMAA spheres. After calcinations to remove completely PSMAA, monodisperse mesoporous titania spheres were obtained, displaying an average particle size of about 130 nm and a pore size distribution centered around 4 nm.

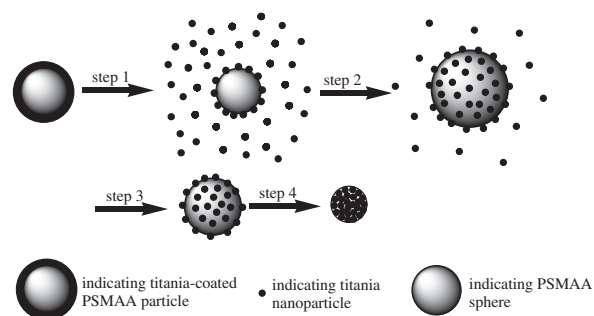


Figure 1. Schematic diagram for the formation of titania/PSMAA spheres and mesoporous titania spheres.

Mesoporous materials with variable composition, controllable morphologies, and tunable wall structures are of particular interest for catalysis, adsorption, and medicine.¹ Especially, monodisperse mesoporous inorganic spheres in sub-micrometer size have recently received much attention for their potential applications as drug delivery carriers, catalyst supports, and photonic crystals.² Most work in this area, however, has been limited to monodisperse mesoporous silica spheres because they can be readily synthesized in truly monodisperse sizes and in copious quantities by using polymer templates.³

In terms of photonic band gap, titania should provide some immediate advantages over silica due to its relatively high refractive indices. Although various methods have been developed to fabricate spherical mesoporous titania particles,⁴ until now there are only a few reports of the synthesis of mesoporous titania spheres with truly monodisperse sizes.⁵ Recently, some researchers have discovered that the nonporous polymer spheres could serve as a medium in which physical processes or chemical syntheses are performed by swelling the polymer spheres and the subsequent infiltration of monomers or inorganic precursors.⁶ In the present work, a similar strategy was introduced to synthesize monodisperse mesoporous titania spheres in sub-micrometer size by employing monodisperse poly(styrene-*co*-methacrylic acid) (PSMAA) spheres as templates.

Figure 1 shows the overall synthetic procedures for the monodisperse mesoporous titania spheres. First, PSMAA particles were prepared in a colloid medium by following a similar technique reported by Wang et al.⁷ Second, the as-prepared PSMAA spheres were homogeneously coated with titania according to our previous work.⁸ Then the titania-coated PSMAA particles were dispersed in an ethanol/toluene mixed solvent. In this step, the titania coatings composed of nanoparticles were mostly divorced from the surface of PSMAA spheres and redispersed into the mixed solvent. However, a small number of titania nanoparticles still remained on the surface of PSMAA spheres to avoid the destruction of the spherical morphology of the polymer spheres during their

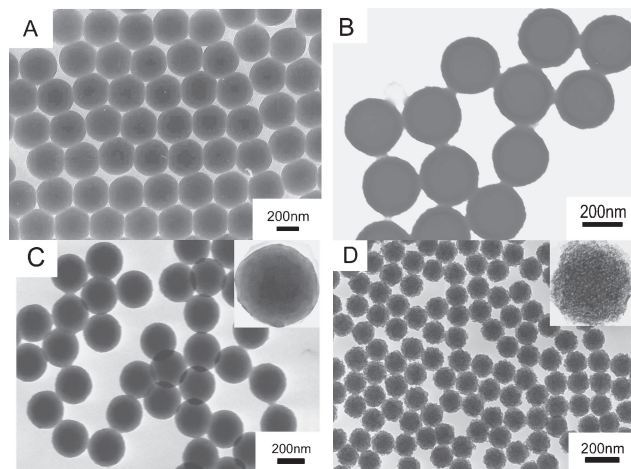


Figure 2. TEM images of (A) PSMAA spheres, (B) titania-coated PSMAA spheres, (C) titania/PSMAA composite spheres, and (D) mesoporous titania spheres. The insets of Figures 2C and 2D show the structures of an individual sphere of titania/PSMAA and mesoporous titania, respectively.

swelling process, as shown in step 1 of Figure 1. Subsequently, the redispersed titania nanoparticles infiltrated gradually into the swollen polymer spheres to create uniform titania/PSMAA composite particles (step 2). After being harvested by centrifugation (step 3), the composite particles were calcined to remove completely the polymer phase, and monodisperse mesoporous titania spheres were finally obtained (step 4).

Figure 2 shows the TEM images of the particles obtained at different synthesis stages. The PSMAA spheres in Figure 2A displayed a well-developed sphere morphology and a highly monodisperse particle size distribution. The mean particle diameter was determined to be approximately 220 nm. More-

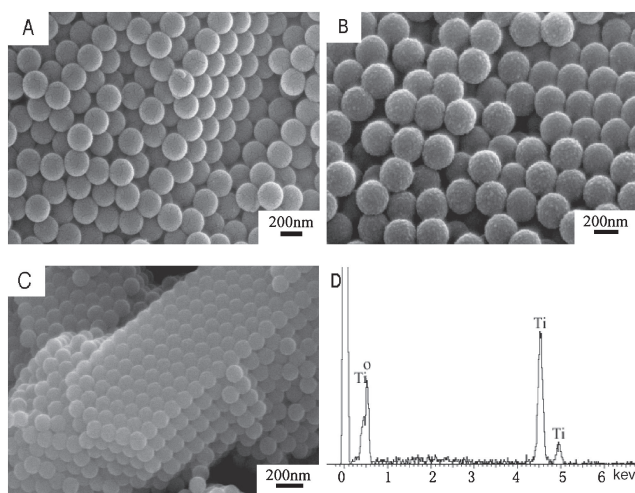


Figure 3. SEM images of monodisperse (A) PSMAA particles, (B) titania/PSMAA composite particles, and (C) mesoporous titania spheres. Figure 3D shows the typical EDX spectrum of the mesoporous titania spheres.

over, both the monodispersity and the spherical morphology of the PSMAA particles were well retained when their surface was coated with uniform titania layers of 44 nm in thickness, as shown in Figure 2B. After being treated with the ethanol/toluene mixed solvent, the titania-coated PSMAA particles transformed from a core-shell structure to a non-core-shell architecture (Figure 2C) while keeping their high monodispersity and perfect morphology. A high-magnification TEM image of an individual titania/PSMAA particle (inset of Figure 2C) revealed that the titania nanoparticles were uniformly distributed in the PSMAA sphere. The average particle size of the titania/PSMAA composite spheres in Figure 2C was about 270 nm, larger than that of the pure PSMAA particles in Figure 2A. This indicated that titania nanoparticles successfully infiltrated into the swollen PSMAA spheres in the presence of the mixed solvent. Finally, mesoporous titania spheres with a high monodispersity were obtained by calcining the uniform titania/PSMAA composite particles. As presented in Figure 2D and its inset image, the as-prepared mesoporous titania spheres have a good spherical morphology and a well-defined nanochannel structure. The average particle size of the titania spheres was about 130 nm.

Figures 3A–3C exhibit the SEM images of the as-prepared PSMAA, titania/PSMAA composite, and mesoporous titania particles. Their average diameters estimated from the SEM images were 220, 270, and 132 nm, respectively, which agreed well with the TEM images in Figure 2. Moreover, the three types of particles all had a perfect spherical morphology and a high monodispersity. The EDX spectrum in Figure 3D revealed that, after calcinations of titania/PSMAA composites, only two elements of titanium and oxygen were detected. The absence of peaks corresponding to carbon suggested that the PSMAA polymer matrix was completely removed from the composite samples by calcinations. The resultant particles were composed of titania with mesoporous structures. Moreover, the high monodispersity of the mesoporous titania spheres was thought to be replicated from the PSMAA spheres. The XRD pattern of the

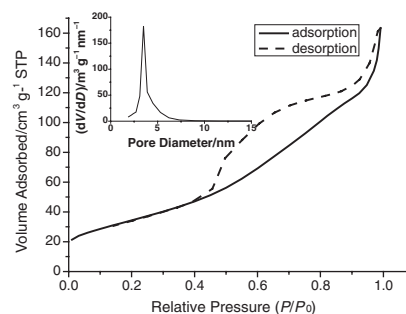


Figure 4. N₂ adsorption-desorption isotherms of the mesoporous titania spheres. The inset shows the pore size distribution determined from the desorption branch.

as-prepared mesoporous titania spheres in Figure S1 showed a typical anatase phase (JCPDS file No. 21-172) with a high crystallinity and an estimated average crystallite size of around 5.1 nm.⁹

Nitrogen sorption isotherms of the monodisperse titania spheres along with their Barret-Joyner-Halenda (BJH) pore size distribution plot are demonstrated in Figure 4. The results indicated that the monodisperse titania spheres were basically mesoporous with the pore size predominantly less than 8 nm and a pore size distribution centered around 4 nm. The BET specific surface area and pore volume of the titania spheres were measured to be 125 m² g⁻¹ and 0.216 cm³ g⁻¹, respectively. It was implied from the above result that the mesopores mainly originated from the interstices among the interconnected titania nanoparticles, which was in good agreement with the TEM observations.

In summary, an effective strategy was introduced to synthesize monodisperse mesoporous titania spheres in sub-micrometer size. The as-prepared titania spheres possessed fantastic structural characteristics such as high monodispersity, good spherical morphology, well-developed mesoporous structure as well as large specific surface area and pore volume, which are highly desired for applications in areas of energy conversion and environmental cleanup.

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