Communications

Facile Synthesis of Hollow Anatase Titania Prepared by Charged Polymeric Nanosphere Template

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Introduction

Two main synthetic routes have been employed to produce inorganic-coated polymer nanoparticles.[1-11] The first approach is to precipitate to form a thin inorganic shell of hydrolyzed metal oxide precursors onto the polymeric template.[1-3] The second approach is a layer-by-layer (LBL) deposition technique to form alternate layers of oppositely charged inorganic and organic species on the core materials.[2,12,13] Various inorganic materials, including silica, titania, zirconia, clay and iron oxide, are used as a coating material.[14-17] Among them, titania has attracted a great deal of recent attention, due to their application in catalysis, photovoltaics and photoelectronics.[18-21] Titania-coated particles are particularly useful as catalysts,[22,23] white pigments[24] and electrophoretic particles.[25,27] These inorganic-coated polymer nanoparticles have been also used to prepare inorganic hollow nanoparticles, which are prepared by removal of the polymer core either by etching in solution or by calcination at high temperature.[28,29]

Hollow titania spheres have been prepared by the LBL manipulation of preformed inorganic nanoparticles onto

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polymeric colloidal.[1,30] Recently, templated syntheses of hollow titania spheres was reported based on sulfonated polystyrene particles, which were prepared by seed emulsion polymerization, followed by treatment in concentrated sulfuric acid.[31] We also reported the preparation of hollow titania nanospheres, based on the cationically-charged copolymer core, comprised of styrene, butyl acrylate and cationic [2-(methacryloxy) ethyl]trimethyl ammonium chloride (MOTAC), was prepared by soap-free emulsion polymerization. Cationically-charged polystyrene nanospheres were prepared by using an ionogenic initiator of 2,2'-azo bis(2-methylpropionamidine)dihydrochloride (AIBA). The formation of the organic-inorganic hybrids was achieved by adsorption of titania through the hydrolysis of titania precursor.

In the present study, to achieve the rapid and sufficient adsorption of inorganic precursor species onto the surfaces of polymer nanospheres, we synthesize positively-charged, monodisperse polymeric cores which are easily associated with negatively-charged inorganic titania precursors by charge density matching. To enhance the charge density of the polymer nanospheres, the polymer cores were prepared by surfactant-free emulsion copolymerization of methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDMA) and methacryloxyethyltrimethyl ammonium chloride (MOTAC) in the presence of azo bis(isobutylamidine) hydrochloride (AIBA) as an initiator. Unlike our previous study, the component monomers used in the present work are all acrylic, relatively-large amount of the cationic MOTAC monomer can be incorporated within the polymer backbone, which results in the increase in the charge density onto the surface of the polymer core in an attempt to achieve the sufficient adsorption of negatively-charged titania and obtain hollow titania nanospheres with adequate shell thickness.

Results and Discussion

Monodisperse polymer nanospheres, composed of methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDMA) and methacryloxyethyltrimethyl ammonium
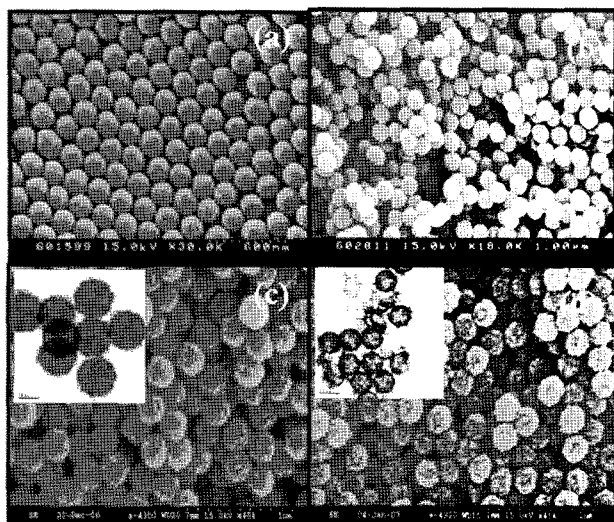
Figure 1. SEM images of (a) poly(MMA-*co*-EGDMA-*co*-MOTAC) nanoparticles, (b) NH₂-poly(MMA-*co*-EGDMA-*co*-MOTAC) particles, (c) titania-coated polymer nanospheres, and (d) hollow titania nanospheres. The insets represent the TEM images of each sample.

Figure 2. Wide angle X-ray diffraction (WAXD) patterns of the (a) titania-coated polymer nanospheres and (b) hollow anatase titania, calcined at 500 °C.

chloride (MOTAC) [poly(MMA-*co*-EGDMA-*co*-MOTAC)], were successfully prepared by soap-free emulsion polymerization. The electrophoretic mobility measurement of the poly(MMA-*co*-EGDMA-*co*-MOTAC) nanospheres gave a ζ-potential of +80 mV and electrophoretic mobility of 9.2 mV and 7.69×10^{-5} cm²/Vs at a neutral pH and below. To enhance the cationic charge density of the surfaces of the nanospheres, the aminolysis reaction was conducted *via* nucleophilic attack on the carbonyl carbon of poly(MMA-*co*-EGDMA-*co*-MOTAC) to form a positively charged tetrahedral intermediate. The nanospheres after the aminolysis reaction were denoted as NH₂-poly(MMA-*co*-EGDMA-*co*-MOTAC) nanospheres. The ζ-potential and electrophoretic mobility of the NH₂-poly(MMA-*co*-EGDMA-*co*-MOTAC) was 28.7 mV and 2.37×10^{-4} cm²/Vs. In Figures 1(a) and (b), we observed the mono-disperse polymeric nanospheres with a diameter in the range of 170-220 nm. Dynamic light scattering (DLS) was also used to measure the size and distribution of the polymerized particles. The DLS data showed that the breadth of the distribution of the particles, obtained by the polydispersity value of the particles was relatively narrow, indicating that the particles were almost monodisperse.

Titania shell was successively deposited onto the positively-charged surfaces of the poly(MMA-*co*-EGDMA-*co*-MOTAC) nanospheres by the consecutive precipitation of the negatively-charged, hydrolyzed titania precursors. Poly(MMA-*co*-EGDMA-*co*-MOTAC) nanospheres with an average diameter of approximately 190 nm was used as a template.

During the adsorption of titania precursor on the surfaces of the polymer cores, we added PVP to prevent the particles from coagulating each other. By exploring the positively-charged polymer nanospheres, the negatively-charged tita-
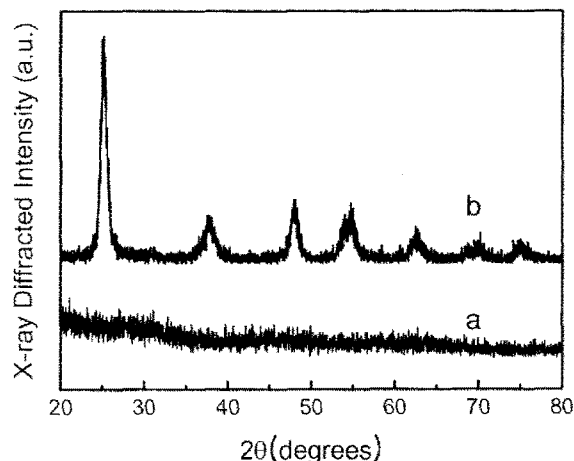
nia precursors can be rapidly adsorbed to form titania shells with a uniform thickness. The deposition and condensation reaction of the titania precursor were carried out for 24 h to ensure their uniform coating onto the polymer surfaces. During the reaction, the negatively-charged titania precursors were deposited onto the positively-charged surfaces of polymer nanospheres by electrostatic interactions and the hydrolyzed titania precursors were then thermally condensed to form a three-dimensional infinite network-like gel of -Ti-O- bonds through a solid rearrangement reaction. Because a low concentration of titanium butoxide was used to make the sol, its gelation proceeded slowly in a bulk solution. However, the adsorbed sol particles located on the surfaces of the polymer nanospheres increased their local concentration, which led to an increase of the gelation speed of the titania sols to form the titania shells on the polymer nanospheres.[32] In Figures 1(c), the average diameter of the titania-coated polymer nanospheres was approximately 230 nm, which estimated the average thickness of the titania shell as approximately 25 nm. It was also found that the thin layer of the titania shells was composed of fine titania particles.

These polymer core/titania shell nanospheres were transferred to a furnace and heat-treated in air at 500 °C to remove the polymeric core by calcination. The average diameter of the hollow titania nanospheres was approximately 180 nm which was reduced by 24%, as compared with one measured from the titania-coated polymer core/shell nanospheres. The main reason of this shrinkage may be due to the crystallization of the adsorbed titania precursors during the heat-treatment, together with the removal of the polymer cores.

Figure 2 showed the wide angle X-ray diffraction (WAXD) patterns of the (a) titania-coated polymer nanospheres and (b) hollow titania, calcined at 500 °C. In Figure 2(a), no

peak was observed in the range of $20° \leq 2\theta (degree) \leq 80°$. Since the polymer core was purely amorphous, the XRD data indicated that the titania shells coated onto polymer cores were also amorphous. In Figure 2(b), we found a series of sharp and strong Bragg peaks which appeared due to the anatase phase of the titania crystals in the shells.

The data indicated that the amorphous titania gels, adsorbed on the polymer core surfaces was crystallized during the calcination at a high temperature. We also found the trace of Bragg's peaks due to the rutile crystalline phase of titania crystal, but its amount was almost negligible. Based on the peak width of the most intense peak at $2\theta \sim 25°$, which was assigned as (101) peaks of anatase type titania crystal, we estimated the apparent size of the titania crystal using Scherrer equation, which was about 13.8 nm. Upon annealing at 800 °C, rutile phase became predominant. However, most of the hollow spheres were ruptured because the thin titania shells were not robust at extremely high temperatures.

The polymer cores could be also removed by immersing in a selective solvent, e.g. tetrahydrofuran, but the morphology of the solvent-etched hollow titania was slightly distorted during solvent etching because the titania shells was too thin to be maintained without any deformation. The shell of the calcined hollow titania was composed of small titania crystallites, as clearly demonstrated in Figure 1(d).

In summary, the nanoparticles with the organic core and the inorganic shells have been synthesized by using stepwise reactions such as the soap-free emulsion copolymerization of the cationic colloidal core and the thermal condensation of the titania shell. Monodisperse and stable cationic nanoparticles were prepared by the introduction of cationic comonomer as a template. The positive charge on the spheres thus ensures not only the rapid capture of the negatively charged titania precursor to form titania shell, but also the thin-layer deposition of the titania precursors onto the polymer surface with uniform thickness.

Supporting Information: Experimental procedure for the syntheses of poly(MMA-co-EGDMA-co-MOTAC), NH₂-poly (MMA-co-EGDMA-co-MOTAC), polymer core/titania shell, hollow titania, their FTIR and TGA, DLS data. The materials are available via the Internet at http://www.polymer.or.kr.

References

(1) A. Imhof, *Langmuir*, **17**, 3579 (2001).
(2) L. Wang, T. Sasaki, Y. Ebina, K. Kurashima, and M. Watanabe, *Chem. Mater.*, **14**, 4827 (2002).
(3) Z. Liang, A. S. Susha, and F. Caruso, *Adv. Mater.*, **14**, 1160 (2002).
(4) L. Qi, J. P. Chapel, J. C. Castaing, J. Fresnais, and J. F. Berret, *Langmuir*, **23**, 11996 (2007).
(5) M. L. Breen, A. D. Dinsmore, R. H. Pink, S. B. Qadri, and B. R. Ratna, *Langmuir*, **17**, 903 (2001).
(6) K. P. Velikov and A. van Blaaderen, *Langmuir*, **17**, 4779 (2001).
(7) C. Tedeschi, F. Caruso, H. Moehwald, and S. J. Kirstein, *Am. Chem. Soc.*, **122**, 5841 (2000).
(8) X. Shi, T. Cassagneau, and F. Caruso, *Langmuir*, **18**, 904 (2002).
(9) J. Cho, J. F. Quinn, and F. Caruso, *J. Am. Chem. Soc.*, **126**, 2270 (2004).
(10) A. Rogach, A. Susha, F. Caruso, G. Sukhorukov, A. Kornowski, S. Kershaw, H. Mohwald, A. Eychmuller, and H. Weller, *Adv. Mater.*, **12**, 333 (2000).
(11) D. Wang and F. Caruso, *Chem. Mater.*, **14**, 1909 (2002).
(12) F. Caruso, *Adv. Mater.*, **13**, 11 (2001).
(13) F. Caruso, X. Shi, R. A. Caruso, and A. Susha, *Adv. Mater.*, **13**, 740 (2001).
(14) F. Caruso, R. A. Caruso, and H. Moehwald, *Science*, **282**, 1111 (1998).
(15) R. A. Caruso, A. Susha, and F. Caruso, *Chem. Mater.*, **13**, 400 (2001).
(16) D. R. Hwang, J. Hong, J. Lee, and S. E. Shim, *Macromol. Res.*, **16**, 329 (2008).
(17) S. J. Han, K. Shin, K. D. Suh, and J. H. Ryu, *Macromol. Res.*, **16**, 399 (2008).
(18) V. P. S. Perera, P. K. D. D. P. Pitigala, P. V. V. Jayaweera, K. M. P. Bandaranayake, and K. J. Tennakone, *Phys. Chem. B*, **107**, 13758 (2003).
(19) H. Wang, C. C. Oey, A. B. Djurisic, M. H. Xie, Y. H. Leung, K. K. Y. Man, W. K. Chan, A. Pandey, J. M. Nunzi, and P. C. Chui, *Appl. Phys. Lett.*, **87**, 023507/1 (2005).
(20) P. Hoyer, *Langmuir*, **12**, 1411 (1996).
(21) J. Yu, L. Zhang, B. Cheng, and Y. Su, *J. Phys. Chem. C*, **111**, 10582 (2007).
(22) A. Hanprasopwattana, S. Srinivasan, A. G. Sault, and A. K. Datye, *Langmuir*, **12**, 3173 (1996).
(23) X. Song and G. Lian, *J. Phys. Chem. C*, **111**, 8180 (2007).
(24) W. P. Hsu, R. Yu, and E. Matijevic, *J. Colloid Interf. Sci.*, **156**, 56 (1993).
(25) T. H. Kim and Y. K. Kwon, *Mol. Cryst. Liq. Cryst.*, **464**, 727 (2007).
(26) C. A. Kim, M. J. Joung, S. D. Ahn, G. H. Kim, S. Y. Kang, I. K. You, J. Oh, H. J. Myoung, and K. H. Baek, *Synth. Met.*, **151**, 181 (2005).
(27) A. Ofir, T. Dittrich, S. Tirosh, L. Grinis, and A. Zaban, *J. Appl. Phys.*, **100**, 074317/1 (2006).
(28) X. Song and L. Gao, *Langmuir*, **23**, 11850 (2007).
(29) T. H. Kim, K. H. Lee, and Y. K. Kwon, *J. Colloid Interf. Sci.*, **304**, 370 (2006).
(30) C. W. Guo, Y. Cao, S. H. Xie, W. L Dai, and K. N. Fan, *Chem. Commun.*, **6**, 700 (2003).
(31) Z. Yang, Z. Niu, Y. Lu, Z. Hu, and C. C. Han, *Angew. Chem., Int. Ed.*, **42**, 1943 (2003).
(32) B. B. Lakshmi, P. K. Dorhout, and C. R. Martin, *Chem. Mater.*, **9**, 857 (1997).