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Fabrication of titania nanostructures using core–shell polymer nanofibers from block copolymers as templates

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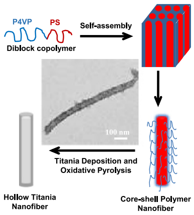
GRAPHICAL ABSTRACT



Titania nanotubes and nanospheres were fabricated from functional core-shell polymer nanofibres as sacrificial templates. The polymer nanofibres were isolated from a cylinder-forming polystyrene-*block*-poly(4-vinylpyridine) block copolymer using selective-swelling approach.

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ABSTRACT

Core–shell polymer nanoobjects obtained from a polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) block copolymer (BCP) were used as a sacrificial template for the preparation of titania nanotubes and nanospheres. The core–shell nanoobjects with a shell composed of P4VP blocks were used as hosts to carry out the sol–gel synthesis of titania using titanium isopropoxide as the precursor. The loading of precursor on the polymer nanoobjects could be done in the solution (dispersion) state as well as in solid state, that is, after immobilizing of BCP templates on the substrate. The titania/polymer nanoobjects thus fabricated were calcined at high temperature to produce pure titania nanoobjects. The formation of the titania nanoobjects was confirmed by the energy filtered transmission electron microscopy (EFTEM) analysis.

1. Introduction

Recently, hollow nanostructures have attracted significant attention because of their potential applications in biochemistry, catalysis and material sciences, etc. [1]. Among different inorganic nanostructures, hollow titania nanoobjects are of special interest because of their usage in photocatalysis, gas sensors, dye-sensitized solar cells, optics, and so forth [2–6]. A number of different methods such as hydrothermal synthesis, electrospinning and template chemistry have been used for the fabrication of hollow titania nanostructures [5–18]. Well-defined templates, in particular, allow the fabrication of tailor-made materials with specific

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shapes and structural properties and, hence, have received significant attention [14–17]. Among the template based approaches, soft templates have been particularly interesting because of the possibility of their easy removal. For instance, the use of cylindrical molecular brushes reported by Müller and co-workers was one such soft template approach [19]. In this case, cylindrical molecular brush had a core–shell–corona morphology such that the shell forming blocks were used as host for titania synthesis. However, the synthesis of such cylindrical molecular brushes is complex and difficult to upscale for application purposes.

An alternative strategy for preparing structures similar to cylindrical molecular brushes involves self-assembly approach using block copolymers. Depending upon the degree of polymerization (N), volume fraction of the constituting blocks (φ) and the Flory Huggins interaction parameter (χ), the block copolymers undergo self-assembly to form well-ordered structures such as bcc packed spheres, hexagonally packed cylinders and lamellae's. Thus, to obtain nanofibers or nanotubes, cylinder forming block copolymers could be used, such that cylindrical nanodomains can be isolated as individual nanoobjects. The diameter of individual cylinder could be precisely tuned by varying the block copolymer molecular weight and could be as small as 20 nm. However, for obtaining these cylinders in form of individual nanofibers, stabilization of the cylinder-forming minority block is required, for example, by photo- or chemical cross-linking, so that the structure remains unperturbed in the presence of solvent [20–22].

On the other hand, it is possible to isolate BCP nanoobjects, using selective solvent approach, which does not require any additional stabilization (cross-linking) of one of the BCP components. The important prerequisites here are sufficiently high χN value and strong solvent selectivity towards one of the block. Recently, we have shown that in the case of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP), the core–shell type of hairy nanofibers with PS core and hairy P4VP shell could be easily isolated in a solvent selective for P4VP block and without any additional cross-linking step [23,24]. These nanofibers potentially could be functionalized with a range of functional materials driven by the chemically active nature of the P4VP shell. As an example, here, we demonstrate that the core–shell nanofibers, as obtained via selective solvent approach from self-assembled PS-*b*-P4VP block copolymer, can effectively be used for the synthesis of BCP/TiOx core–shell type nanofibers and pure titania one dimensional nanostructures. Moreover, it will be further shown that through a simple heat treatment, the polymeric core–shell nanofiber can be converted into core–shell nanospheres (i.e. BCP spherical micelles) which then can template the formation of titania nanospheres.

2. Experimental

2.1. Materials

PS-*b*-P4VP block copolymer with three different molecular weights, PS(18500)-b-P4VP(40500), PS(38000)-b-P4VP(82000) and PS(85000)-b-P4VP(196000), were procured from Polymer Source, Canada (the numbers indicate the number average molecular weight of the particular polymer block). The volume fractions of the PS and P4VP blocks were such that all were expected to self-assemble into cylindrical morphology composed of PS blocks. The solvents chloroform and methanol were purchased from Sigma Aldrich and were used as received. The titania precursor, titanium tetraisopropoxide (TTIP), was also procured from Sigma Aldrich. Highly polished single-crystal silicon wafers of {100} orientation were used as substrates. The silicon wafers were cleaned with dichloromethane in an ultrasonic bath for 20 min and then further in a 1:1:1 v/v mixture of 29% ammonium hydroxide (Acros), 30% hydrogen peroxide (Merck) and deionized water for 1.5 h at 65 °C, rinsed several times with water and finally dried in an argon flow.

2.2. Fabrication of polymer nanoobjects

PS-*b*-P4VP block copolymer was dissolved in chloroform (a common solvent for both PS and P4VP) at room temperature. The solution was then kept in a saturated vapor atmosphere of chloroform in a closed chamber with a very small opening for slow solvent evaporation. After complete evaporation of the chloroform, block copolymer film was then treated with ethanol which is a selective solvent for P4VP block. This led to swelling of the P4VP matrix phase and isolation of PS cylindrical domains in ethanol as nanofibers. The isolated nanofibers so prepared could be further transformed to nanospheres by refluxing the dispersion of nanofibers in ethanol. The nanofibers dispersed in ethanol (1 mg/ml) were placed in a round bottom flask fitted with a reflux condenser and heated on a hot plate at the boiling point of the ethanol for 48 h. After refluxing for 48 h the dispersion was stored in a glass vial.

2.3. Preparation of titania nanoobjects

Here, we employed two different approaches to fabricate the titania nanoobjects from the PS-*b*-P4VP block copolymer templates. The titanium tetraisopropoxide (TTIP) was used as the precursor. First, the titania sol was prepared by mixing 4.3 mL of TTIP with 4.2 mL of 12.1 M HCl solution in a glass vial. The mixture was placed on a magnetic stirrer for vigorous stirring at room temperature for 10 min, and then 5 mL of ethanol was added while stirring. The formation of the polymer-inorganic hybrid nanoobjects was achieved by two methods, namely "on-substrate" method and "in-solution" method. In the "on-substrate" approach, the polymer nanoobjects were first immobilized on the substrates (silicon wafer or TEM grids) from their methanol dispersion and subsequently treated with the titania sol for 10 min and then washed with ethanol to remove excess of sol and dried with air flow. In "in-solution" method, the titania sol was directly added to the ethanol containing dispersed nanofibers and titania deposition was carried for the next 30 min under stirring. Subsequently, this mixture was drop/spin casted over the requisite substrate. The substrates were then washed with ethanol to remove superfluous titania sol over the substrate and dried with air flow. The titania coated polymer nanofibers (or nanospheres) were calcined in an air furnace at 450 °C for 2 h. An increase of temperature was done stepwise to prevent crumbling of the nanoobjects during heat treatment. This process removes the polymeric components leading to the formation of hollow titania nanofibers or nanospheres.

2.4. Characterization

Scanning electron microscopy (SEM) images were obtained with FEI Quanta 200F with Oxford-EDS system IE 250 X Max 80 equipped with field-emission gun (FEG) electron source. The samples prepared on silicon substrates were viewed under the SEM without any additional coating. Transmission Electron Microscopy (TEM) was performed using a JEOL JEM-2100F transmission electron microscope at an accelerating of 200 kV. Energy Filtered TEM (EFTEM) analysis was performed on Zeiss Libra200 TEM equipped with Omega-type energy filter at 200 kV acceleration voltage using 3-windows method. For mapping of Ti, N, C, O the energy windows of 10 eV, 20 eV, 30 eV, 30 eV were used, respectively at the K-ionization edges of N, C, O and L_{23}-ionization edge of Ti. Specimens for TEM imaging were prepared on the carbon coated copper grid and on silicon or silicon oxide thin films supported by silicon frame (TEMwindows^{TM}) by drop casting method. Dynamic