Hollow Inorganic Nanospheres and Nanotubes with Tunable Wall Thicknesses by Atomic Layer Deposition on Self-Assembled Polymeric Templates**

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Discrete, differently shaped, tailorable, and functional nanoscale building blocks based on a variety of materials are expected to be useful in future engineering at the nanometer scale, and require facile techniques for their design, preparation, tailoring, and manipulation. As prototypical architectures, hollow nanospheres and -tubes with tunable diameters and wall thicknesses could be of considerable interest for a variety of applications, including electronics and sensors, drug release, fluid transportation, and even nanoscale structural parts.[1–4] A straightforward approach is based on coating spherical and rodlike templates with the desired material, followed by removal of the template.[1,5–8] Many types of spherical templates have been used, of which polystyrene latex particles[9–12] and silica spheres[13,14] are among the most common. Some examples of rodlike templates for hollow nanotubes are nanowires,[15] tobacco mosaic viruses,[11] metal-salt crystals,[16] organic crystals,[17] and membranes with straight pores.[18] It is worth noting that the synthesis of rodlike templates typically requires different materials and methodologies compared to spherical templates. Here, we combine three concepts in a novel manner. We use block copolymer self-assembly as a general approach for the synthesis of both spherical and rodlike discrete templates, allowing tunable diameters. Secondly, using aluminium oxide (Al_2O_3) as a prototypical inorganic coating, we demonstrate that atomic layer deposition (ALD)[19–21] allows a novel type of continuous, tunable, and conformal coating for discrete polymer templates compared to previously used techniques.[22] Finally, we demonstrate that the thermal decomposition of the polymer template yields hollow inorganic nanospheres and -tubes with tunable diameters and wall thicknesses. In principle, such inorganic structures could in turn be coated with other inorganic materials by ALD, where even high-temperature processes can be used as the organic core matter has been removed.

Block copolymers consist of well-defined mutually repulsive polymeric blocks that are covalently connected, thus leading to competitive interactions and self-assembled nanostructured materials.[23,24] Complementary physical interactions, which are dealt with in supramolecular chemistry,[25] can be applied to bind further structural moieties within block copolymers to achieve additional hierarchy levels,[26] prepare discrete nanoscale objects,[24,27] or direct the self-assembly of inorganic materials.[28–32] In particular, hydrogen-bonded polymer–surfactant complexes of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) and alkyl phenols, such as pentadecyl phenol (PDP) and dodecyl phenol (DDP), lead to discrete PS-*b*-P4VP nanorods with a PS core and P4VP corona.[27,33,34] The advantages of such a supramolecular approach include: i) reduction of the glass-transition temperature (T_g) of both phases ($T_g(PS) \approx 67\,°C$; $T_g(P4VP/PDP) \approx$ room temperature)[35] to allow shear alignment at moderate temperatures for improvement of the self-assembled structures; and ii) preparation of PS-core–P4VP-corona nano-objects by simple dissolution of PDP. Electroless deposition using Pd and adsorption of CdSe nanoparticles allows granular inorganic coatings on the PS-*b*-P4VP rods.[22] Instead of granular coatings, continuous and conformal coatings are produced by ALD, and therefore enhanced properties resulting from suppression of grain or domain boundaries could be expected. ALD is a gas-phase deposition technique based on saturative surface reactions between alternately supplied gaseous precursors and builds up coatings in fractions of a monolayer, thereby allowing sub-nanometer precision in coating thickness combined with conformal growth, even on complex-shaped substrates.[19,21] In this work, PS-*b*-P4VP nanospheres and -rods, with optional molecular reinforcement by poly(2,6-dimethyl-1,4-diphenyl oxide) (PPE),[34] are used as templates for Al_2O_3 coatings. The continuous inorganic coating gives

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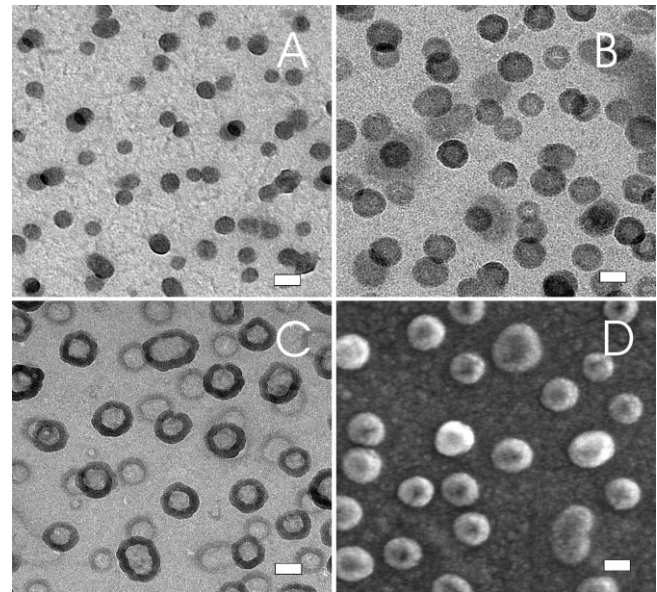Nijenborgh 4, 9747 AG, Groningen (The Netherlands)

structural stability that prevents collapse upon removal of the template (by heating), thus allowing hollow interiors.

The general route for the synthesis of hollow nanospheres and nanotubes is depicted in Figure 1. First, a diblock-copolymer–amphiphile complex is prepared based on an alkylphenol (e.g., PDP or DDP) and PS-*b*-P4VP using a common solvent and subsequent solvent evaporation, where there is nominally one phenol hydrogen-bonded to each pyridine group of PS-*b*-P4VP (Fig. 1A and B).
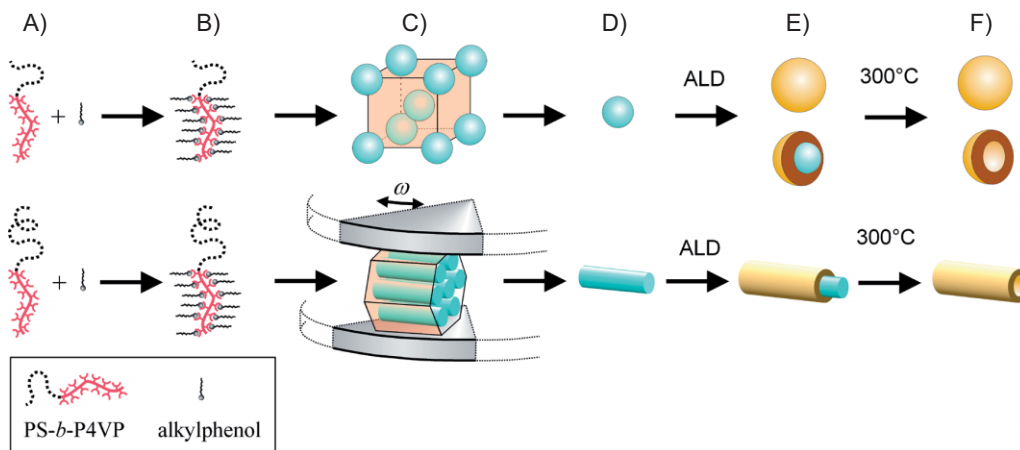
This polymer/surfactant complex self-assembles into various organized bulk structures depending on the volume ratio between PS (potentially including PPE) and P4VP/alkylphenol (Fig. 1C).[36,37] PS-*b*-P4VP with approximately equal block lengths leads to a cylindrical morphology of PS in a P4VP/alkylphenol matrix.[27] Imposing shear leads to well-aligned and elongated cylinders (bottom part of Fig. 1c).[33] When the PS block is shorter, PS spheres are formed in a P4VP/alkylphenol matrix (top part of Fig. 1C). The matrix phase can be selectively swollen by placing the bulk material in ethanol, thereby cleaving the phenols which leads to the formation of a dispersion of discrete nanospheres and -rods with a PS core and a P4VP corona (Fig. 1D). For simplicity, the core–corona structure is not depicted in Figure 1D, but details have been reported elsewhere.[27,33,34] Transmission electron microscopy (TEM) studies showed nanospheres (Fig. 2A) and nanorods (Fig. 3A) with a narrow diameter-distribution.

Subsequently, the polymeric nanoparticles are coated with a thin layer of Al_2O_3 using ALD.[19,21] Recently, polymers have been coated by ALD-grown inorganic thin films, on substrates such as flat films,[38–44] particles,[45–47] fibers[48] and even bottles.[49] The critical issue in coating the nanoscale polymeric templates is whether or not sufficiently low-temperature processes can be selected to avoid destruction of the template. To coat the polymeric nanoparticles, trimethylaluminum
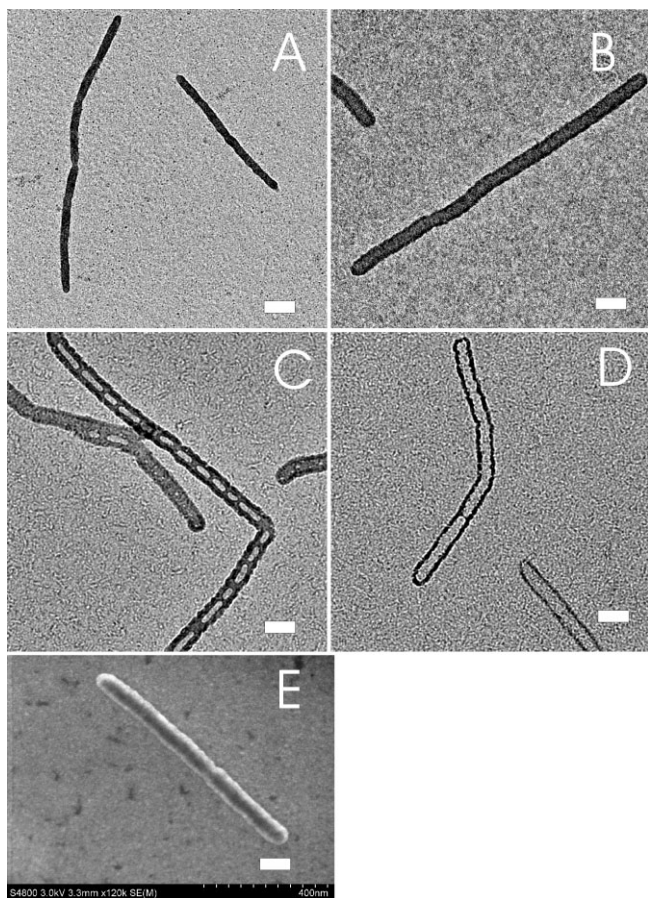

Figure 2. A–C) TEM images of ALD-coated nanospheres at each step of the fabrication process: A) Polymer spheres consisting of a PS core and a P4VP corona. B) Polymer spheres coated with an ALD-grown Al_2O_3 layer (200 cycles). C) Hollow Al_2O_3 spheres fabricated by thermal decomposition of the polymer template. D) Scanning electron microscopy (SEM) image of hollow Al_2O_3 spheres. The scale bar is 50 nm.

$(Al(CH_3)_3$, TMA) and water (H_2O) are selected as the Al and O precursors for the growth of Al_2O_3 thin films. This is apparently the most ideal ALD process and allows film deposition at low temperatures. Furthermore, the films deposited with this process are known to adhere exceptionally well, even to polymer substrates. TEM images show spheres and rods that have a core/shell structure (Figs. 2B and 3B). The

Figure 1. A–F) Route for the synthesis of hollow inorganic nanospheres and nanotubes. A) Mixing of a PS-*b*-P4VP block copolymer with an alkylphenol. B) Formation of a hydrogen-bonded complex. C) Self-assembly into a spherical or cylindrical nanostructure. The morphology is largely determined by the block lengths of the block copolymer. Application of shear leads to well-aligned and elongated cylinders. D) Discrete spherical and rodlike objects with a PS core and P4VP corona are obtained by dissolving the alkylphenol in ethanol. For simplicity, the PS-core–P4VP-corona structure is not depicted. E) The objects are coated with a thin continuous layer of Al_2O_3 by ALD using successive cycles of trimethylaluminum and water. F) Decomposition of the polymer template at 300 °C results in hollow inorganic nanospheres and nanotubes.
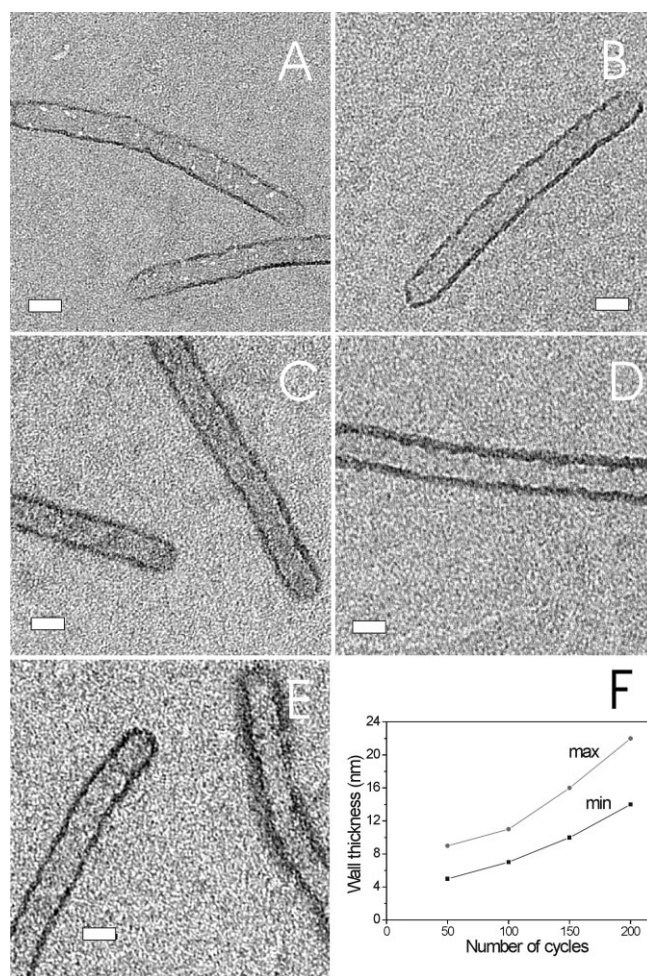
Figure 3. A–D) TEM images of ALD-coated nanorods at each step of the fabrication process. A) Polymer nanorods with a PS core and a P4VP corona. B) Polymer nanorods coated with an ALD-grown Al_2O_3 layer (150 cycles). C) Partially emptied Al_2O_3 tubes fabricated by thermal decomposition of the polymer template for 2 h at 200 °C. D) Completely emptied Al_2O_3 tubes obtained by thermal decomposition for 4 h at 300 °C. E) SEM image of completely emptied Al_2O_3 tubes. The scale bar is 100 nm.

core is the polymer template and the shell is the ALD-grown inorganic film. The contrast between core and shell originates from the higher electron density of Al_2O_3 compared to the polymer. The contrast in the TEM images is enhanced when the samples are heated to 300 °C (Figs. 2C and 3D). At this temperature the polymer is removed, probably by decomposition to small gaseous molecules. At a lower temperature, the polymer is only partially removed (Fig. 3C). Removal of the polymer by heating indicates that the inorganic shell is permeable to the gaseous decomposition products. The total decomposition of the polymer at 300 °C in a nitrogen atmosphere is somewhat surprising because thermogravimetric analysis generally shows these polymers are stable to temperatures above 300 °C.[50] Thermogravimetric analysis, however, is usually performed on the bulk polymer, and extrapolation of bulk properties to nanoscale objects is thus not always valid. The different behavior may be related to the specific surface area of nano-objects, which is significantly higher than that of their bulk counterparts. The resulting materials are hollow Al_2O_3

nanospheres (Fig. 2C and D) and Al_2O_3 nanotubes (Fig. 3D and E).

The thickness of the inorganic wall can be controlled by the number of ALD cycles. Figure 4A, B, C, and D shows images of the nanotubes made using 50, 100, 150, and 200 deposition cycles, respectively. The wall thickness increases with the number of cycles. The nonlinear relation between wall thick-

Figure 4. A–E) TEM images of completely emptied Al_2O_3 tubes fabricated using an increasing number of deposition cycles. A) 50 cycles. B) 100 cycles, C,E) 150 cycles. D) 200 cycles. The scale bar is 50 nm. F) The minimum and maximum thickness of the Al_2O_3 walls as a function of the number of deposition cycles.

ness and number of cycles could be due to inaccuracies in the determination of the edge of highly curved surfaces by TEM or overestimation of film thicknesses at a low number of cycles, originating from the roughness of the substrate.[51] Two types of nanotube walls are found: tube walls with sharp edges and tube walls with diffuse edges. Figure 4E shows both types of tubes in the same image (the left tube has sharp edges; the right tube has diffuse edges). For the calculation of the wall thickness (Fig. 4F) only tubes with sharp edges are taken into

account. The diffuse edges indicate an Al_2O_3 film with a lower density. This could be due to a non-ALD type of growth, when the reactants (H_2O and TMA) are simultaneously present and react to form Al_2O_3. The presence of H_2O during the TMA pulse, even after purging with N_2, could potentially originate from the porosity of the first Al_2O_3 layers due to irregularities in the underlying polymer template.[43] Tubes with a diffuse Al_2O_3 coating could be more porous, allowing water to penetrate to the polymeric template. P4VP is a hygroscopic polymer and could attract and retain traces of H_2O that react with TMA in the following reaction cycle.

The construction of inorganic nanoparticles with hollow interiors was demonstrated by coating self-assembled polymeric nano-objects with a thin Al_2O_3 layer, followed by removal of the polymer template upon heating. The morphology of the nano-object (i.e., spherical or cylindrical) is controlled by the block lengths of the block copolymer. The thickness of the Al_2O_3 wall is controlled by the number of ALD cycles. We foresee polymer self-assembly as a general route for the synthesis of templates for hollow nanomaterials with various controlled morphologies and sizes. Also, ALD is an attractive technique for the synthesis of inorganic nanoparticles.

Experimental

Preparation of Polymeric Nanospheres: PS-*b*-P4VP diblock copolymer M_n(PS) = 18 600 g mol^{-1}, M_n (P4VP) = 55 800 g mol^{-1} and $M_w/M_n = 1.26$, Polymer Source, Inc. M_n: number-average molecular weight: M_w: weight-average molecular weight) was used as received for the synthesis of nanospheres. 3-Pentadecylphenol (PDP) (Aldrich, 98 %) was purified by recrystallizing twice from petroleum ether. The samples were prepared by mixing stoichiometric amounts of PS-*b*-P4VP and PDP in analysis grade chloroform (concentration = 1 wt %). After stirring for 1 day, the solution was poured in a Teflon cup and the solvent was allowed to evaporate slowly overnight. The sample was annealed for 2 days in vacuum (10^{-3} mbar, 1 bar = 10^5 Pa) at 150 °C. The sample was then dissolved in ethanol. One drop of the nanosphere suspension was placed on a carbon-coated copper grid and the solvent was evaporated. The copper grid was placed in a vacuum oven (10^{-7} mbar) at 70 °C for 2 days to ensure that no PDP was adsorbed on the spheres.

Preparation of Polymeric Nanorods: PS-*b*-P4VP diblock copolymer (M_n(PS) = 21 400 g mol^{-1}, M_n (P4VP) = 20 700 g mol^{-1}, $M_w/M_n = 1.13$, Polymer Source, Inc.) was used as received for the synthesis of nanorods. To reinforce the nanorods, homopolymer poly(2,6-dimethyl-1,4-diphenyl oxide) (PPE) was used ($M_w = 25 700$ g mol^{-1}, $M_w/M_n = 1.37$), also acquired from Polymer Source, Inc. 4-Dodecylphenol (DDP) was purchased from Aldrich as a mixture of isomers and was used as received. The nanorods were prepared according to the procedure described by van Zoelen et al. [34].

Atomic Layer Deposition: The Al_2O_3 films were deposited by ALD at 80 °C using TMA and H_2O as the Al and O precursors, respectively. Carbon-coated copper grids covered with nanospheres and nanorods were used as substrates for ALD. The depositions were performed in a flow-type F-120 ALD reactor (ASM Microchemistry Ltd, Finland) [52] that was operated under a pressure of 10 mbar using N_2 as the carrier and purging gas. The precursors were evaporated in their external reservoirs at room temperature and led to the reactor using needle and solenoid valves. The precursor vapors were supplied alternately on the polymeric nanostructures, and the reaction chamber was purged with N_2 after each precursor pulse. One growth cycle consisted of a TMA pulse (2 s), a N_2 purge (60 s), a H_2O pulse (0.5 s), and a N_2

purge (150 s). The growth cycle was repeated 50, 100, 150, or 200 times. The polymer template was removed by thermal decomposition at 200 °C or 300 °C in a N_2 atmosphere.

Electron Microscopy: Bright-field TEM was performed using a Tecnai 12 transmission electron microscope operating at an accelerating voltage of 120 kV. The SEM images were acquired with a Hitachi S-4800 Field Emission scanning electron microscope. The analysis of the wall thickness from TEM images was carried out using Gatan DigitalMicrograph 3.8.2 software on at least 20 nanotubes.

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