

Responsive Hybrid Nanotubes Composed of Block Copolymer and Gold Nanoparticles

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Received April 8, 2009; Revised Manuscript Received May 13, 2009

ABSTRACT: We demonstrate the facile fabrication of high aspect ratio nanotubes from responsive block copolymer, polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP), and *in situ* grown gold nanoparticles. PS-*b*-P2VP nanotubes are fabricated by template-assisted assembly by utilizing cylindrical pores of porous alumina membranes followed by its dissolution. Solvent annealing was employed to facilitate ordered phase separation of the block copolymer with in the nanotube structure, followed by *in situ* formation of gold nanoparticles in the P2VP domains occupying the inner and outer shell of the nanotubes. Owing to the pH-sensitive nature of P2VP block, which exhibits a coil to globule transition above pH 3.6, the PS-*b*-P2VP–gold nanoparticles hybrid nanotubes show reversible changes in topology, size (up to 25%), and collective plasmon resonance appearance. We suggest that PS-*b*-P2VP–gold nanoparticles hybrid nanotubes with their pH-responsive properties, large surface-to-volume ratio, and through open pore can find intriguing applications in sensing and microfluidic systems.

Introduction

One-dimensional (1D) organic nanostructures such as nanorods, nanotubes, nanowires, and nanobelts have been of intense interest due to their unique physical properties originating due to the confinement on characteristic length scale of the components (e.g., radius of gyration, single domain).^{1–4} Fabrication of 1D organic nanotubes or nanorods structures has been achieved by a variety of methods such as template-assisted,⁵ self-assembly in the liquid phase,⁶ electrospinning,⁷ and inductive coupled plasma reactive ion etching.⁸ Among these fabrication methods, the template-assisted technique has been widely investigated due to favorable traits such as easy control over the shape, size, and the diversity of materials that can be used.^{9–11} Among various nanostructures, polymer nanotubes and nanorods can be assembled by wetting, vacuum, and spin-based infiltration of polymer melt or solution into nanocavity.¹²

On the other hand, as known, responsive materials and structures which can readily change their properties (optical, electrical, mechanical) or shape are extremely important for a wide variety of applications such as sensors, actuators, adaptive surfaces and interfaces, and drug delivery.^{10,13,14} Encapsulating and direct growth of inorganic nanoparticles into compliant organized polymeric matrices has been suggested for both re-inforcement and sensing purposes and demonstrated on many occasions.^{15–17} *In situ* formation of metal nanoparticles in soft polymer matrices such as multilayered polyelectrolyte films, ultrathin polymer films, and block copolymers has been demonstrated using synthetic and biomacromolecules which can selectively bind, nucleate, and reduce nanoparticles.^{18–22}

On the other hand, block copolymers, one of the most promising materials for responsive structures, are comprised of two or more chemically distinct, and often immiscible, polymer chains covalently bound together.^{23,24} In the simplest case of diblock copolymer, incompatibility between two dissimilar

blocks drives the system to self-organize by microphase separation to minimize the interfacial energy between the dissimilar blocks.^{25,26} The structural changes in a responsive polymer/ nanoparticle hybrid 1D nanostructure to external stimuli can be translated to readable optical signal if characteristic optical signature is presented.^{27,28} Wang et al. fabricated microphaseseparated diblock copolymer nanorods by infiltration of polymer melt into anodic alumina membrane template with high temperature (230 °C) and investigated the topology of nanorods at different pH.²⁹ The responsive nanorods exhibited a change in the topology to mesoporous state upon exposure to acidic environment. However, the reversibility of topology, size, and the optical signature of the composite nanotubes with external pH remain to be investigated.

Here, we demonstrate the facile fabrication of hybrid 1D nanostructures comprised of pH-responsive block copolymer, polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP), with encapsulated gold nanoparticles. We successfully fabricate PS-*b*-P2VP core—shell type nanotubes with controlled level of microphase separation of dissimilar blocks and large surface-to-volume ratio by solvent annealing under physical confinement.³⁰ *In situ* reduction of gold nanoparticles in P2VP domain of these nanotubes was used to decorate the inner wall and outer shell of the nanotubes. Such an approach results in uniform distribution of nanoparticles and block copolymer. Furthermore, we demonstrate that the pH-responsive nature of P2VP is translated to a reversible change in topology and optical properties of the block copolymer nanotubes.

Results and Discussion

As known, P2VP is a weak cationic polyelectrolyte exhibiting a coil-to-globule transition above pH 3.6.³¹ PS($M_w = 102000$) – P2VP($M_w = 97000$) diblock copolymer (PDI = 1.12) utilized in this study can be dissolved in common solvent, tetrahydrofuran (THF), and form lamellar phase. Under the physical confinement

Published on Web 06/09/2009

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Figure 1. Fabrication process of PS-*b*-P2VP–gold nanoparticles nanotubes.



Figure 2. (a, b) SEM images of PS-*b*-P2VP–gold nanoparticles hybrid nanotubes, (c) cross section of nanotubes, and (d) inner structure of nanotubes.

in the nanopores of the anodic alumina membranes, PS-*b*-P2VP forms tubular structure along the channel with the lamellae parallel to the walls of porous alumina as was demonstrated by Russell et al. (Figure 1).³² Nanotubes with aspect ratio up to 20 (about 250 nm of diameter and ~5 μ m of length) can be fabricated by spin-assisted infiltration of PS-*b*-P2VP from THF solution followed by solvent annealing and complete dissolution of the alumina membrane (see Experimental Section).^{9,33,34} It has been demonstrated that the infiltration and subsequent solidification of a polymer into the porous template results in either hollow nanotubes or solid nanorods depending on the wetting behavior of the polymer with the walls of the template.³⁵

In fact, SEM images show PS-*b*-P2VP nanotubes fabricated in this study with diameter of 250 nm corresponding well to the pore diameter of the membrane (Figure 2a,b). The microphase separation of the PS and P2VP domains is clearly revealed by the cross-sectional SEM images (Figure 2c). For a polymer which readily spreads, the templating results in long nanotubes whereas in the case of limited spreading it results in short nanorods. PS-*b*-P2VP in THF exhibits high wettability to PAMs, thus resulting in block copolymer nanotubes. Comparing to the nanorod structures frequently demonstrated for these block copolymers, nanotubes possess not only a larger surface-to-volume ratio but also the through channels along the long axis, applicable for the microfluidic system.³⁰

However, the confinement of the lamellar structures with discrete dimension of 30 nm per domain parallel to the walls of the pores results in small through pores. It is known that during the initial deposition, due to the fast solvent evaporation, the block copolymer freezes into fingerprint patterns when spincoated on flat substrate which can be annealed to achieve ordered microphase separation.^{33,36–38} We employed solvent annealing in



Figure 3. (a, b) TEM images of PS-*b*-P2VP–gold nanoparticles hybrid nanotubes, (c) UV–vis absorption spectra of PS-*b*-P2VP nanotubes and PS-*b*-P2VP–gold nanoparticles hybrid nanotubes, and (d) EDS spectrum indicating the presence of Au in polymer nanotubes.

which PS-*b*-P2VP nanotubes were exposed to THF vapor for 24 h to enable ordered microphase separation.³³ Following the solvent annealing, the structure evolves in which the P2VP domains with higher affinity to hydrophilic alumina wall occupy the inner wall and outer shell (30 nm each) with the PS domain (60 nm) located in between the P2VP domains (Figure 2c).

Gold nanoparticles were formed by selective reduction inside in P2VP domains of block copolymer nanotubes by exposing them to the gold salt solution (tetrachloroauric acid) for 15 h. AuCl₄⁻ ions bind to the protonated pyridine units of the P2VP resulting in pyridinium salt.^{18,19} Subsequently, nanotubes are washed in Nanopure water and are immersed into aqueous solution of reducing agent (sodium citrate), resulting in the formation of the gold nanoparticles in P2VP domains (Figures 2 and 3).³⁹ Gold nanoparticles were found to grow uniformly on the inner wall and outer shell of nanotubes (Figure 2d). The presence of gold nanoparticles in the P2VP domains further supports the suggested structure, in which the P2VP domains form the inner wall and outer shell of the nanotubes with PS domain separating them. The energy dispersive spectroscopy (EDS) confirms the presence of gold nanoparticles in the nanotubes (Figure 3d).

High-resolution TEM image shows that the gold nanoparticles with the average diameter of 15 ± 2 nm are uniformly distributed along the entire length of the block copolymer nanotubes (Figure 3a,b). The presence of gold nanoparticles in PS-*b*-P2VP nanotubes results in an appearance of a strong absorption band at 540 nm due to the surface plasmon resonance of individual gold nanoparticles and possibly some nanoparticle aggregates (Figure 3c).⁴⁰

Because of their pH-sensitive nature, P2VP domains swell upon exposure to pH below 3.6 due to protonation of nitrogen in pyridine group which causes electrostatic repulsion leading to swelling of the polymer chains.^{29,41} This transformation leads to the dramatic change in the topology of nanotubes in response to the external pH (Figure 4a–c). We employed pH 2 (coil state) and pH 7 (globule state) to study the morphology changes and optical response of PS-*b*-P2VP–gold nanoparticles hybrid nanotubes. In neutral state, one can observe the smooth surface of PS*b*-P2VP nanotubes uniformly decorated with gold nanoparticles (Figure 4a). When PS-*b*-P2VP–gold nanoparticles hybrid nanotubes are exposed to pH 2, inner wall and outer shells of the P2VP domains swell, forming grainy structure (Figure 4b). The inset of Figure 4b shows the expanded nanotubes structure due to the swelling of P2VP domains. It has been demonstrated that P2VP exhibits a 100% volumetric swelling upon exposure to pH 2.⁴¹ Apparently, the mechanical integrity of nanotubes is preserved by the glassy PS block. Upon exposure of the PS-*b*-P2VP porous



Figure 4. (a) SEM images of PS-*b*-P2VP–gold nanoparticles hybrid nanotubes, (b) after exposed to pH 2, and (c) exposed to pH 7.

nanotubes to the neutral condition (pH 7 solution), the highly grainy morphology of nanotubes is apparently recovered to the initial smooth surface (Figure 4c).

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Apart from the morphology rearrangement, the diameter of PS-*b*-P2VP nanotubes is altered upon exposure to pH 2 (Figure 4a–c). The diameter of PS-*b*-P2VP nanotubes was 240 ± 5 nm after neutral solution but increases up to $300 \pm$ 10 nm after swelling at pH 2. Assuming that the entire increase in the diameter (60 nm) results from the swelling of P2VP domains (120 nm), the linear swelling of the P2VP domains is estimated to be 50%. After exposure to neutral solution (pH 7), P2VP blocks are deprotonated and the nanotubes shrink back to the initial size.

The morphological changes caused by exposure of PS-*b*-P2VP nanotubes to pH 2 resulted in a 23 nm red shift of the plasmon resonance of the encapsulated gold nanoparticles (Figure 5a). We suggest that, in the case of PS–P2VP nanotubes studied here, swelling of the P2VP blocks causes the aggregation of the gold nanoparticles at the outer surface. The aggregation of nanoparticles increases coupling of plasmon resonances, resulting in the red shift.^{40,42,43} It is worth noting that the effect observed is in striking contrast to previous studies of P2VP–gold nanoparticles thin films which observed a significant blue shift upon swelling of the P2VP domains.^{28,44} The blue shift was associated with the increased separation between the gold nanoparticles uniformly dispersed in the planar films in contrast to the decreasing distances in constrained curved shell conditions for PS–P2VP nanotubes studied here.

Moreover, the exposure of nanotubes to neutral solution results in the further gold nanoparticles rearrangement due to topology recovery resulting in a reverse change in plasmon resonances. This reverse change is manifested as a 15 nm blue shift of the plasmon peak (Figure 5). Changes observed here can be utilized for subsequent cycling between pH 2 and pH 7 exposures resulting in alternating, closely reproducible red—blue shifts. These optical responses are completely reversible for multiple times (Figure 5b).

For further understanding of the topology changes and gold nanoparticles rearrangement of PS-*b*-P2VP nanotubes with external pH, which causes plasmon resonance shift, we employed PS-*b*-P2VP micelles. PS-*b*-P2VP dissolved in toluene, selective solvent for PS, forms micelles with P2VP core and PS shell. The micelle film is prepared by spin-coating on a silicon substrate, and gold nanoparticles were reduced by the same method described previously. AFM images show the micelle structure



Figure 5. (a) UV-vis absorption spectra of PS-*b*-P2VP-gold nanoparticles hybrid nanotubes exposed to pH 7 and pH 2 solutions. (b) Reversibility of spectra at pH 7 and pH 2.



Figure 6. (a) AFM topographical (top) and phase (bottom) images of PS-*b*-P2VP micelle structure spin-coated film on Si substrate with gold nanoparticles and (b) after exposed to pH 2. (c) Schematic of morphology changes of PS-*b*-P2VP–gold nanoparticles micelle structure under pH treatment.

of PS-*b*-P2VP thin film with gold nanoparticles in the P2VP domains (core of the micelle) (Figure 6a). The dimpled structure of PS-*b*-P2VP micelles after exposure to pH 2 solution and the presence of gold nanoparticles on the surface are clearly visible in Figure 6b. Upon exposure to pH 2 solution, P2VP cores with gold nanoparticles swell, resulting in dimpled structure of the micelle film and exposure of the gold nanoparticles to the surface as shown in schematic (Figure 6c).

In conclusion, we demonstrated the facile fabrication of pHresponsive nanotubes composed of PS-*b*-P2VP–gold nanoparticles which exhibit a reversible change in the plasmon resonance position. We suggest that the large surface-to-volume ratio of nanotubes and open through central pore maximizes their interaction with environment, thus enhancing their tunable response to external stimuli which can be extremely beneficial in microfluidics and biosensing.

Experimental Section

Fabrication of PS-b-P2VP Nanotubes with Gold Nanoparticles: Block Copolymer. PS(102K)-b-P2VP(97K) was purchased from Polymer Source Inc. Porous alumina membranes (PAMs) were purchased from Whatman (Anodisc 47), and the average pore size was 243 ± 5 nm with 60 μ m total thickness. Nanotubes were formed by infiltration of 2 wt % PS-b-P2VP in THF into PAMs three times using spin-coating. Then nanotubes are exposed to tetrahydrofuran (THF) vapor for 24 h. Nanotubes in PAMs were immersed in 0.75 wt % of tetrachloroauric acid (Aldrich) for 24 h. Gold nanoparticles were selectively reduced in P2VP domain in aqueous reducing agent 0.015 wt % (sodium citrate) solution. Then nanotubes were released from PAM templates by dissolving in 40 wt % of KOH solution. Nanotubes were separated by sonication for 15 min, centrifuged (5000 rpm), and then redispered in Nanopure water 5 times to remove residual KOH salt.

Optical Response. Nanotubes with gold nanoparticles are exposed pH 2 solution for 40 min, and UV-vis absorption spectra of nanotubes were obtained using LEICA Microsystem

DM4000 with a CRAIC point-shot spectrometer. Then nanotubes are exposed to pH 7, following which the plasmon resonance spectra were collected. It is worth mentioning that the optical response was time dependent, saturating at nearly 30 min as concluded from monitoring transformation at different times. The data reported here were collected after exposure for 40 min to ensure the complete response. The sequence was repeated multiple times to study the repeatability of and reversibility of the response.

SEM, TEM, and AFM Analysis. A field-emission scanning electron microscopy (FESEM, LEO 1530) was used to investigate the morphology of PS-*b*-P2VP nanotubes with gold nanoparticles. A JEOL 100CX-2 electron microscope was exploited at 100 kV. AFM scanning was conducted on a Dimension 3000-Nanoscope IIIa microscope (Digital Instruments). AFM images were obtained in tapping mode according to the procedure adapted in our lab.⁴⁵ AFM scanning was conducted with the rate of 0.8–1.0 Hz for surface areas of 1 μ m × 1 μ m. The AFM images of at least several different areas of the sample were collected, and the representative images were selected. Silicon nitride tips were used with tip radii between 20 and 50 nm and spring constants ranging from 0.01 to 50 N m⁻¹.

Acknowledgment. This work is supported by National Science Foundation (NSF-CMS-0709586) and Air Force Office of Scientific Research.

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