Fabrication of Polyaniline Silica Nanotubes and Closed Polyaniline Nanotubes Using a Template of Silica Nanotube

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Polyaniline silica nanotubes (PANI@SNT) were prepared by in situ polymerization of anilinium ion adsorbed on the surface of silica nanotubes (SNT), which acted as a template. After polymerization, the silica templates were intensively removed with HF solution to give closed polyaniline nanotubes (PANI–NT). Interestingly, the PANI@SNT showed pH-responsive redox reversibility.

The fabrication of one-dimensional nanostructures of conjugated polyaniline (PANI) by a simple method has received much interest because of their unique properties, which relate to its oxidation and protonation state.[1] And also they have potential applications such as nano-sized transistors,[2] displays,[3] and chemical sensors[4] or actuators.[5]

Among the known nanomaterials, nanotubes are known to play an important role in optoelectronic nanodevices since their surface can easily be altered to accommodate specific optoelectronic properties. In the past few years, many inorganic nanotubes composed of silicon, titanium oxide, vanadium oxide, and silica have been synthesized, and many approaches to fabricating organic nanotubes have also been presented. On the contrary, only a limited number of nanotubes composed of conjugated polymers have been reported. In this context, considerable efforts have been made on the synthesis of nanotubes of conjugated polymers. So far, nanotubes of conjugated polymers with uniform dimensions have been obtained mainly by a template-synthetic method with "Track-etch" membrane or anodic aluminum oxide, or anodic manganese oxide as a template.[6] Recently, Huang and Wan have reported the synthesis of PANI nanotubes generated through a self-assembly process in the presence of azobenzenesulfonic acid (ABSA) as a dopant, which acted as a template.[7] However, to our best knowledge, nanotubes of conjugated polymers have not yet been fabricated using a template of silica nanotube (SNT). Herein, we report the fabrication and characterization of polyaniline silica nanotubes (PANI@SNT) and polyaniline nanotubes (PANI–NT) using a template of silica nanotube.

The cholesterol-based gelator **1** (Chart 1) was synthesized as described previously.[8] The silica nanotube with a diameter of ca. 200 nm and several micrometers in length was prepared by sol–gel condensation of tetraethoxysilane (TEOS), which was used as the silica precursor, in a cholesterol-based organogel system (Figure S1).[9] The organogel template was completely removed by calcination. The PANI wall was formed by in situ polymerization of anilinium ion adsorbed on the outer surface of silica, probably due to the fact that initially filled water molecules in the inner space of nanotube prevent access of anilinium ion into the inner surface of silica, although we did not have any evidence. The overall synthetic procedure of PANI@SNT and PANI–NT is illustrated in Scheme 1. In this procedure, the silica surfaces serve as templates for adsorption of aniline monomers as well as counter ions for doping of the synthesized PANI. The positively charged anilinium ions in acidic conditions (pH 3) were adsorbed on the negatively charged surface of the silica nanotube through electrostatic interactions. The aniline monomers electrostatically complexed to the silica surface were then polymerized by ammonium persulfate (APS) as an oxidizing agent at room temperature. After polymerization, the silica templates were intensively removed with HF solution to give a PANI–NT. The detail of PANI@SNT and PANI–NT fabrication was described in Supporting Information.[9]

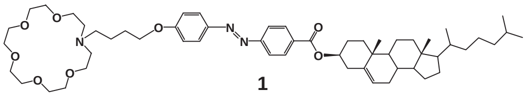

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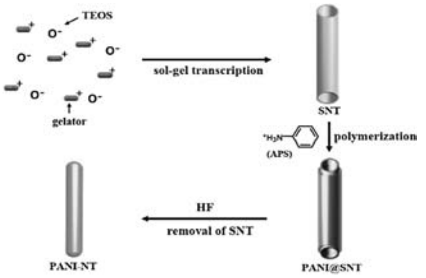
Chart 1.



Scheme 1. Schematic representation of PANI@SNT and PANI–NT fabrication by template polymerization.

The morphologies of PANI@SNT and PANI–NT were investigated with a field-emission scanning electron microscope (FE-SEM) and a transmission electron microscopy (TEM) (Figure 1). After polymerization, the SEM image of the resultant showed a tubular structure, which was similar to that obtained from sol–gel transcription in the gel phase of **1**. The diameter of PANI@SNT was ca. 250 nm and the length was more than 5 µm (Figure 1a). Particularly, the TEM image of PANI@SNT displayed a hollow structure as nanotube with uniform dimensions of size and diameter. The diameter and length of the PANI@SNT are consistent with the SEM image, and the wall thickness of PANI@SNT was ca. 24 nm (Figure 1a + inset). Whereas the SEM image of the PANI–NT showed that the hollow cavity was significantly reduced and closed after washing with HF solution. The diameter of PANI–NT range from 60 to 90 nm, and the length was less than 2 µm (Figure 1b). The template-removing step can result in the disorder or destruction of the nanostructure or affect the chemical structure of PANI. In this reason, this may result from the contraction of thin

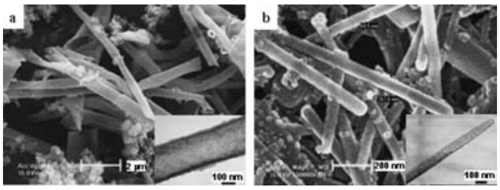


Figure 1. FE-SEM images of (a) PANI@SNT synthesized by the template method and (b) PANI–NT in which the template was completely removed by HF. The insets of (a) and (b) are the TEM images of PANI@SNT and PANI–NT, respectively.

PANI layers on the surface of silica when removed the template. Nevertheless, the TEM image revealed that the PANI–NT retained a tubular structure (Figure 1b + inset). The solution of PANI–NT was green in color, it was very stable in that no precipitation was observed after a few months, and the size of PANI–NT was almost unchanged. Interestingly, the dispersion in water could be freely diluted, probably due to the fact that polyaniline can principally form colloid, indicating the effective stabilization of emeraldine salt in aqueous environment by the HF. According to thermogravimetric analysis (TGA), polyaniline on the surface of PANI@SNT was 14 wt %, whereas the PANI–NT contains 57 wt % of polyaniline, obviously because the silica template was removed by washing with HF solution (Figure S2).[9] For the comparison of the thermal stability of PANI–NT, polyaniline was also purchased from Aldrich. Figure S2 shows that the heat stability of the PANI film improved because the film has a tubular nanostructure.[9] The thermal stability of polyaniline in this type was also observed in the polyaniline/CNT composite nanotube.[10]

The molecular structures of the PANI@SNT and PANI–NT were studied by FT-IR. The absorption bands at 1591 and 1507 $\mathrm{cm^{-1}}$ for PANI@SNT and 1564 and 1484 $\mathrm{cm^{-1}}$ for PANI–NT, can be assigned to the C=C stretching of the quinoid and benzenoid rings in the emeraldine salt of PANI. The C–N stretching mode at 1307 $\mathrm{cm^{-1}}$ and the absorption band of N=Q=N (Q representing the quinoid ring) at 1117 $\mathrm{cm^{-1}}$ were observed in the PANI–NT. In the PANI–SNT, the C–N stretching mode at 1291 $\mathrm{cm^{-1}}$ was observed. Whereas the absorption band of N=Q=N was not observed because owing to the strong band of Si–O–Si at 1085 $\mathrm{cm^{-1}}$, which originated from the SNT, concealed the absorption band of N=Q=N from view (Figure S3).[9]

To elucidate the electronic structure, UV–vis absorption spectra of PANI@SNT were investigated with varying pH of the dispersion solution. The PANI@SNT at pH 3 exhibits a relatively featureless adsorption band gradually decreasing from high to low energy in the UV–vis absorption spectrum. Whereas, as the pH of the solution increased up to 12, the new strong absorption band at 560 nm emerged (Figure 2). This result indicated that PANI was completely transformed from the emeraldine salt form to the emeraldine base form by the deprotonation of PANI with increasing pH. The photograph shows the color change of the PANI@SNT against the pH of the solution (Figure 2 + inset). The solution of the PANI@SNT at pH 3 was in green. The color changed from green to blue and violet at increased pHs of 7 and 12, respectively. This result strongly supports the view again that PANI has been fully deprotonated to the emeraldine base form. Interestingly, the color change was fully reversible, as decreasing the pH of the solution. In addition, the color change remained over several cycles of deprotonation–protonation. These results clearly indicate that the PANI@SNT is stable in operating conditions and could be applied as a pH-responsive sensing material.

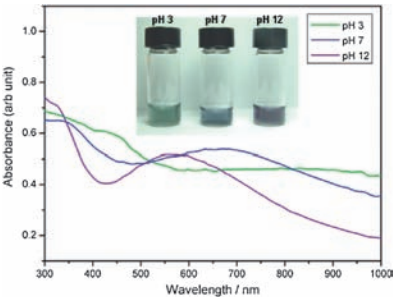


Figure 2. UV–vis spectra of PANI@SNTs for different pH values. The inset is photograph of PANI@SNTs.

In summary, we have fabricated PANI@SNT and PANI–NT using a template of SNT, in which the PANI@SNT showed a well-defined nanotubular structure with a diameter of ca. 250 nm and several micrometers in length, whereas the PANI–NT showed significantly reduced and closed nanotubular structure with diameters of 60–90 nm and less than 2 µm in length. The PANI@SNT also showed pH-responsive redox reversibility. These findings may lead to development of a new type of tailor-made pH-responsive sensing system built by in situ polymerization of anilinium ion adsorbed on the silica surface.

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