The controlled preparation of cross-linked polyphosphazene nanotubes of high stability *via* a sacrificial template route†

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Received (in Montpellier, France) 18th December 2009, Accepted 8th February 2010
First published as an Advance Article on the web 5th March 2010
DOI: 10.1039/b9nj00774a

We report on the controlled preparation of cross-linked poly(cyclotriphosphazene-co-4,4′-sulfonyldiphenol) (PZS) nanotubes using Ag nanowires as sacrificial templates. The as-prepared PZS nanotubes have a good chemical stability in concentrated nitric acid and an initial 475 °C thermal decomposition temperature in air.

Tubular nanostructures are an interesting and increasingly important class of materials with a variety of applications, including controlled drug delivery, absorption materials, contaminated waste removal, electrochemistry materials and biomedical devices.[1–9] They can also be used as nanoreactors and nanocontainers due to their inner cavity.[10,11] In this regard, considerable effort has been directed toward organic nanotubes.[12,13] During past decades, organic nanotubes have been synthesized from oligopeptides, block copolymers and a variety of other organic building blocks.[14–17] Many of these nanotubes, however, are formed through non-covalent assemblies and are unstable.[12,17] Although the template method introduced by Martin and Parthasarathy involves the fabrication of polymer nanotubes within the void spaces of porous host materials,[18,19] there is limited information with respect to this method for the production of cross-linked polymers. As a potential material used for nanocontainers and nanoreactors, good stability and controllable morphology are necessary. In comparison with a non-covalent assembly structure or a covalently linear structure, a covalently cross-linked structure is a more effective approach to achieving good stability. Therefore, developing a new and facile route to controllably prepare nanotubes with a cross-linked structure should be an interesting research subject.

Recently, we have pioneered the synthesis of poly(cyclotriphosphazene-co-4,4′-sulfonyldiphenol) (PZS) nanotubes *via* an *in situ* template,[20] exploring a route to cross-linked polymer nanotubes. However the morphology, especially the inner diameter size and shell thickness, of the nanotubes is difficult to control precisely using this method because the amount of *in situ* template produced is directly relative to that of the feeding co-monomers during polymerization. More recently, we reported the controlled preparation of Ag/cross-linked PZS and MWCNTs/cross-linked PZS coaxial nanocables by an *ex situ* template method under mild conditions.[21,22] The shell thickness (PZS) could be easily controlled by changing the feed ratio of core materials to co-monomers. This synthetic strategy inspired us to evaluate whether such a facile route could be applied to cross-linked polyphosphazene nanotubes with a controllable morphology by removing the corresponding templates. Our experimental results are in good agreement with our expectations.

Based on the above idea of using Ag nanowires as an *ex situ* hard template, hexachlorocyclotriphosphazene (HCCP) and 4,4′-sulfonyldiphenol (BPS) as co-monomers, and triethylamine (TEA) as an acid acceptor gave Ag/cross-linked PZS nanocables under ultrasonic irradiation at room temperature. The as-prepared nanocables were then etched with concentrated nitric acid to remove Ag core materials, and cross-linked PZS nanotubes of controlled morphology were successfully obtained. The method offers at least three advantages: (1) the as-prepared polyphosphazene nanotubes have a covalently cross-linked chemical structure; (2) they possess a good chemical stability in acidic condition and a good thermal stability in air; (3) the wall thickness of the nanotubes can be easily controlled, and the inner diameter is completely dependant on the size of the template used.

Fig. 1 illustrates the procedure used for preparing PZS nanotubes. Firstly, Ag nanowires were prepared through soft solution processing.[23] Secondly, using the as-synthesized Ag nanowires as a sacrificial template, active PZS particles, produced in the early stage of polymerization between HCCP and BPS as the assembly units, Ag/PZS nanocables were successfully prepared under ultrasonic irradiation at room temperature. Finally, Ag@PZS nanocomposites and PZS nanotubes could be obtained by controlling the acidolysis time.

Fig. 2 shows representative SEM and TEM images of the as-prepared silver/PZS nanocables in this work. The PZS shell, with a thickness of 150 nm, continuously coats along the axis of the Ag nanowire with a diameter of about 65 nm, which is consistent with our previous report.[22]

Fig. 3(a)–(c) shows SEM and TEM images of the PZS nanotubes obtained from the Ag/PZS coaxial nanocables with a shell thickness of ∼150 nm. After treatment using concentrated nitric acid, the morphology of the PZS nanotubes was not altered, indicating that the as-prepared PZS nanotubes were to some extent inert to degradation and had a high

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† Electronic supplementary information (ESI) available: XRD spectra and TEM images. See DOI: 10.1039/b9nj00774a

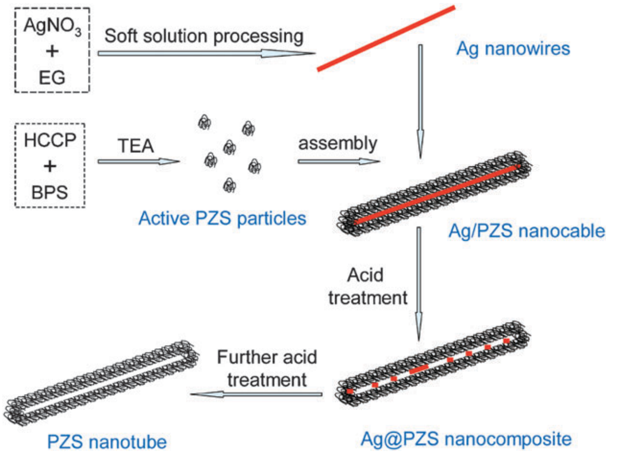

Fig. 1 A schematic illustration of the formation of PZS nanotubes using Ag nanowires as sacrificial templates.

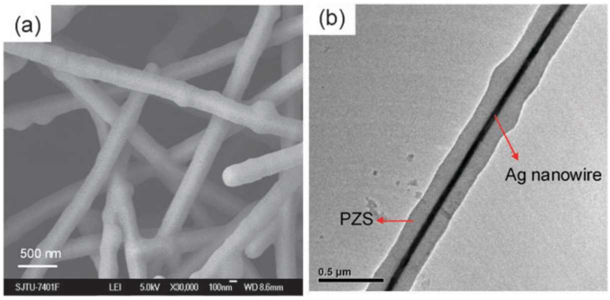

Fig. 2 (a) SEM image of Ag/PZS coaxial nanocables. (b) Typical TEM image of Ag/PZS coaxial nanocables.

chemical stability in acid solution. It should be noted that PZS nanotubes, including Ag nanoparticles (indicated by arrows) in their cavity, could be obtained if the acid treatment time of the Ag/PZS nanocables was set at about 0.5 h, as shown in Fig. 3(b), which demonstrates that the removal of Ag nanowires might experience a process from Ag nanowire to Ag nanoparticle and disappearance. Recently, considerable research effort has been directed towards the synthesis of encapsulated and immobilized metal nanoparticles.[24,25] The encapsulation of these metal nanoparticles inside a capsule or in a tube would lead to the creation of novel catalytic systems. This method in the present study might provide a simple and effective route to preparing metal-filled PZS nanotube composites with a high metal filling ratio. After a 6 h acid treatment, the Ag nanowires were completely removed and true PZS nanotubes were obtained from the corresponding Ag/PZS nanocables, as shown in Fig. 3(c). Only C, O, P, S and Cl could be seen in the EDX spectrum shown in Fig. 3(d), indicating the complete removal of Ag nanowires from the Ag/PZS nanocables. Support for this notion is provided by the contrast photograph shown in the inset of Fig. 3(d). Obviously, the ethanol solution of Ag/PZS nanocables appears light yellow (the color was decided by Ag nanowires) before acid treatment. After a 6 h acid treatment, the resulting products dispersed in ethanol solution are ivory white.

The complete removal of metallic Ag from the corresponding Ag/PZS nanocables was further confirmed by XRD. As shown in Fig. S1 (see the ESI†), before acid treatment, all reflections could be readily indexed to a face-centered cubic phase of silver with a calculated lattice constant a = 4.1 Å, which is in good agreement with the literature value of a = 4.086 Å (JCPDS card file no. 04-0783). After acid treatment, all of these reflections related to silver disappeared and only a wide diffraction peak corresponding to PZS was seen at 14.5°. The fact that the Ag nanowires were successfully removed by concentration nitric acid reveals that the nitric acid could diffuse through the PZS shells and gradually dissolved away the corresponding silver cores. Therefore, the removal of the silver cores in this work was also dependent on the diffusion of nitric acid.

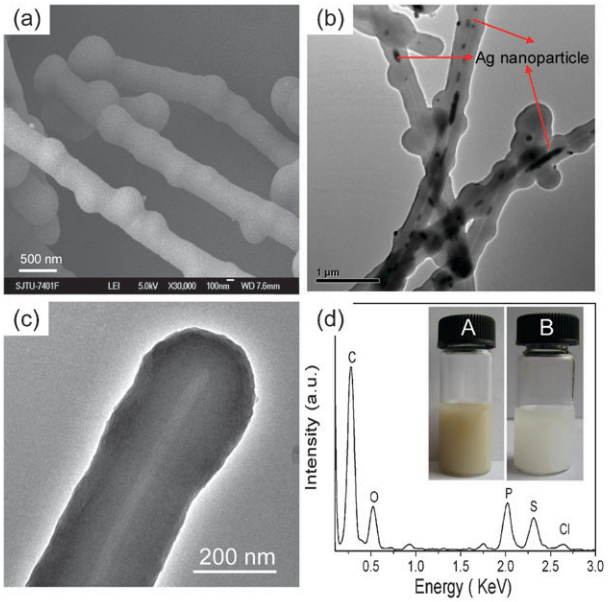

Fig. 3 (a) SEM and (b) TEM images of Ag/PZS nanocables after 0.5 h treatment with concentrated nitric acid. (c) TEM image after 6 h treatment with concentrated nitric acid. (d) The EDX spectrum of Ag/PZS nanocables after 6 h treatment with concentrated nitric acid. The inset of (d) shows the contrast photographs of Ag/PZS nanocables in ethanol solution (A) before and (B) after 6 h treatment with concentrated nitric acid.

Fig. 4 shows the typical FTIR spectrum of the samples after a 6 h acid treatment. For a better comparison, the FTIR spectrum of Ag/PZS nanocables is also shown in Fig. 4. Obviously, all the characteristic absorption signals for the acid treated samples are quite similar to that of the Ag/PZS nanocables. These are the phenylene absorption of the sulfonyldiphenol unit at 1592 and 1487 cm^{-1}, the characteristic absorption of the P=N and P–N of cyclotriphosphazene at 1187 and 881 cm^{-1}, the characteristic absorption of O=S=O at 1295 and 1154 cm^{-1}, and the intense absorption of P–O–Ar at 941 cm^{-1}, proving the occurrence of polycondensation between co-monomers HCCP and BPS. FTIR contrast demonstrates that the highly cross-linked chemical structure of PZS was not damaged after acid treatment, which was further confirmed by elemental analysis. The elemental analysis gives the following results. Calc. for $C_{30}H_{20}ClN_3O_{10}P_3S_{2.5}$ (PZS): C, 45.5; H, 2.5; Cl, 4.5; N, 5.3; P, 11.8; S, 10.1%. Found: C, 45.3; H, 2.6; Cl, 4.0; N, 5.2; P, 11.6; S, 10.0%.

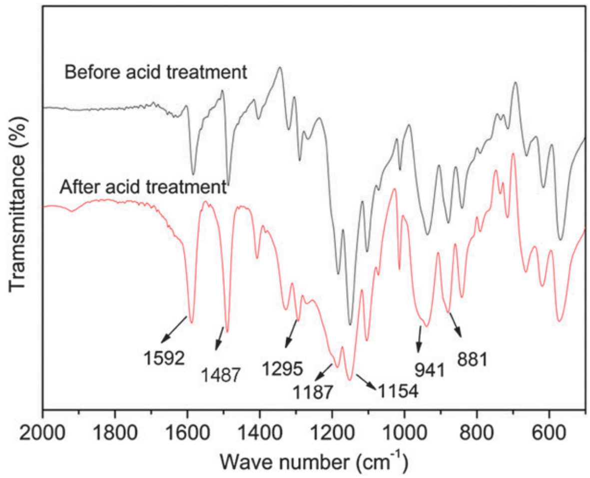

Fig. 4 FTIR spectra of Ag/PZS nanocables before and after a 6 h treatment with concentrated nitric acid.

Based on the FTIR, EDX and EA data, a cross-linked structure of the PZS nanotubes is proposed, as shown in Fig. 5.

To evaluate the thermal stability of the as-synthesized PZS nanotubes, a thermogravimetric experiment was carried out in air. The TGA shows that the initial decomposition of the PZS nanotubes starts at approximately 475 °C, as shown in Fig. 6. This characterization result indicates that the PZS nanotubes possess a good thermal stability that is interrelated with the covalently cross-linked structure of PZS. Similar results were also observed in PZS nanofibers with a highly cross-linked structure.[26] In addition, we also noticed that the initial decomposition temperature of PZS nanotubes was slightly higher than that of Ag/PZS nanocables, indicating that the chemical structure of the PZS nanotubes becomes more stable after acid treatment. The reason for this phenomenon is currently being studied.

It is known that the shell thickness of Ag/PZS nanocables can be readily controlled by tuning the molar ratio of Ag nanowire to co-monomers HCCP and BPS.[22] In this work, the wall thickness of the PZS nanotubes was controlled by changing the co-monomer's dosage in the reaction solution. Fig. S2 shows TEM images of the as-prepared Ag/PZS nanocables and the corresponding PZS nanotubes with a 5 : 1 : 3 molar ratio of Ag nanowire : HCCP : BPS (see the ESI†). Obviously, a PZS nanotube with a wall thickness of about 85 nm was easily obtained from such reaction conditions.

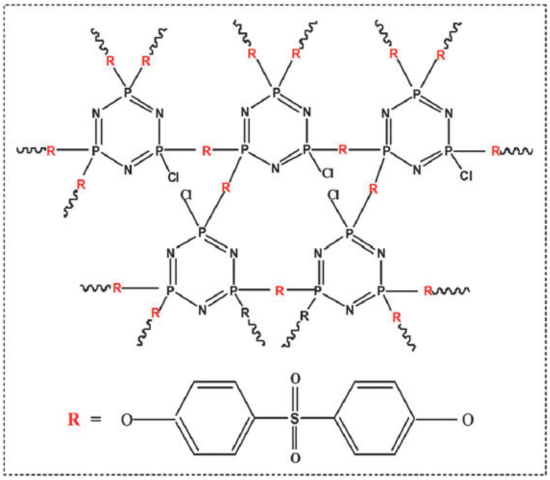

Fig. 5 The highly cross-linked chemical structure of as-synthesized PZS nanotubes.

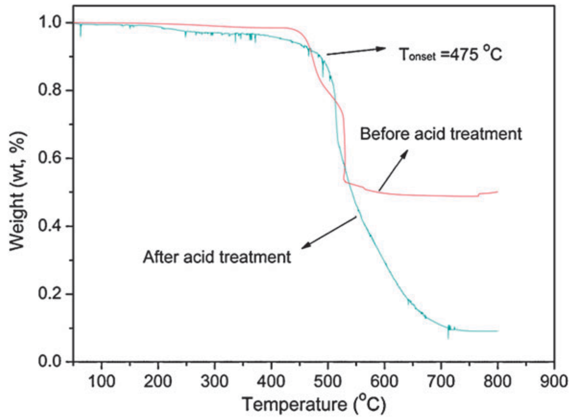

Fig. 6 TGA curves of Ag/PZS nanocables before and after 6 h treatment with concentrated nitric acid.

In conclusion, PZS nanotubes with a highly cross-linked chemical structure were successfully prepared by using Ag nanowires as a sacrificial template. The wall thickness of the nanotubes was controlled by changing the molar ratio of silver to HCCP and BPS co-monomer. The as-prepared PZS nanotubes showed a very good stability to a concentrated nitric acid solution and had an initial 475 °C decomposition temperature in air. We think that the controlled structure and superior stability of the as-prepared PZS nanotubes might make them promising materials for nanoreactors and nanocontainers.

We are grateful to the National Natural Science Foundation of China (no. 20974102, 20804040), the Natural Science Foundation of Henan (no. 092300410048, 092102310051) and for financial support from the Program for New Century Excellent Talents in Universities (NCET).

Experimental

Materials

HCCP (synthesized as described in the literature[27]) was recrystallized from dry hexane followed by sublimation (60 °C, 0.05 mmHg) twice before use (mp = 112.5–113 °C). BPS (purity $>99.5\%$) was obtained from Jiangsu Alonda High-Tech Industry Co., Ltd. (Jiangsu, China) and used as received. Ethylene glycol (EG), silver nitrate, poly(vinyl pyrrolidone) (PVP; $M_w \approx 55\,000$, $n \approx 500$), tetrahydrofuran, ethanol, concentrated nitric acid and TEA were purchased from Shanghai Chemical Reagents Corp. (Shanghai, China) and used without further purification.

Synthesis

The synthesis process of the Ag/PZS nanocables was similar to that reported previously.[22] Briefly, 50.0 mg of Ag nanowires, 62.0 mg of HCCP and 137.0 mg of BPS (in a molar ratio of 5 : 2 : 6) were dispersed in a 50 mL mixture solvent of tetrahydrofuran and ethanol (1 : 1 by volume). After ultrasonic irradiation for 10 min, 4 mL of TEA was injected into the above solution. The solution was then allowed to react for 10 h at room temperature under ultrasonic irradiation (50 W, 40 kHz). As soon as the reaction was complete, the resulting solids were centrifugated and the precipitates washed several times with de-ionized water and ethanol, respectively, to produce the final Ag/PZS nanocables.

PZS nanotubes were obtained by removal of the Ag nanowires using a concentrated nitric acid solution. In this process, as-prepared Ag/PZS nanocables were added to the concentrated nitric acid solution. The Ag etching reaction was then carried out at room temperature under ultrasonic irradiation. After 0.5 h and 6 h, the solution was centrifugated and the precipitates washed several times with de-ionized water and ethanol, respectively. Finally, the resulting products were dried under vacuum to yield PZS nanotubes.

Characterisation

FTIR measurements were conducted on a Perkin-Elmer Paragon 1000 Fourier transform spectrometer at room temperature. Elemental analyses were performed using a Perkin-Elmer 2400-II instrument. SEM measurements were carried out with a JEOL JSM-7401F field-emission microscope. Transmission electron microscopy (TEM) and EDX were performed with a JEOL JEM-100CX microscope operating at 100 kV. The X-ray diffraction (XRD) pattern was recorded on a powder sample using a Bruker D8 Advance instrument with Cu-Kα radiation. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA 7/DX thermogravimetic analyzer in the temperature range from ambient to 800 °C at a heating rate of 20 °C min^{-1} in air.

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