Synthesis and microstructure of silica nanotubes via a coaxial electrospinning route

Lulu Shen, Yunhong Yao, Tianlong Wang, Lan Jia and Song Chen*
College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan, Shanxi, 030024, China
*E-mail: chensong2009@126.com

Abstract. In this study, silica nanotubes (SiO$_2$ NTs) were facilely synthesized via a coaxial electrospinning route. The core-sheath paraffin@PVP-SiO$_2$ nano-fibers (NFs) were firstly prepared through co-axial electrospinning of a sheath-liquid derived from tetraethoxysilane, ethanol, polyvinyl pyrrolidone and hydrogen chloride and a core-liquid of paraffin oil and then sintered at 600\degree C to produce SiO$_2$ NTs. The physicochemical property of the SiO$_2$ NTs was characterized by a SEM machine, a TEM machine and a FT-IR machine. SEM and TEM observations showed that SiO$_2$ NTs had the diameter of 2320±568 nm with a shell thickness of 303±25 nm and a hollow and tubular structure. FT-IR spectrum showed that SiO$_2$ NTs had the characteristic peak of Si-O-Si bonds at 1050 cm$^{-1}$. It was found that the sintering process caused the removal of organic components in paraffin@PVP-SiO$_2$ NFs and the formation of hollow structure in SiO$_2$ NTs.

1. Introduction
Since the discovery of carbon nanotubes (NTs), the tubular nano-materials have received considerable attention in variety of applications such as photo-catalysts[1], drug delivery systems[2], and tissue regeneration[3] because of their unique and one-dimensional hollow structure. Silica (SiO$_2$) NTs are one type of the representative tubular nano-materials. Compared with the well-known carbon NTs, SiO$_2$ NTs have much better advantages such as easy sacrificial template sol-gel synthesis route, low-cost, strong hydrophilicity, ease of surface functionalization, and excellent biocompatibility[4-7]. They have been extensively utilized as supportive platform of photo-catalysts[4], immobilization substrate of enzymes[5], delivery system of therapeutic drugs[6] and cell-supporting scaffolds in tissue regeneration[7].

Sacrificial template sol-gel route is the most favorable method for synthesis of SiO$_2$ NTs since size and morphology of the as-synthesized SiO$_2$ NTs could be well directed by the sacrificed template[8]. In a typical synthesis route, SiO$_2$ NTs are synthesized as the sacrificial template is firstly coated with a layer of SiO$_2$ and then removed with a chemical or physical treatment. A successful establishment of SiO$_2$ layer is crucial to the formation of the subsequent SiO$_2$ NTs. In general, two types of sacrificial templates are available for synthesis of SiO$_2$ NTs, including hard templates and soft templates. Hard templates such as carbon NTs[9] and calcium carbonate[10] have been utilized for synthesis of SiO$_2$ NTs. Carbon NTs are the most favorable hard templates because of their well-defined tubular structure and easy removal by calcination. However, carbon NTs still presented some drawbacks. Firstly, carbon NTs showed a very weak affinity to silicate species due to the lack of functional groups and need to be further modified before establishment of SiO$_2$ layer[9]. Secondly, carbon NTs are very expensive and not suitable for a large-scale production of SiO$_2$ NTs. Soft
templates such as polymer and protein contain many functional groups such as carboxyl groups and amino groups and have much stronger affinity to the silicate species. However, in most cases, the soft templates are not stable in aqueous solution and need to be further cross-linked before establishment of SiO$_2$ layer. For example, the electrosprun PVA nanofibers (NFs) should be cross-linked with glutaraldehyde for synthesis of SiO$_2$ NTs\[11\], while the electrosprun gelatin NFs were cross-linked with carbodiimide for synthesis of SiO$_2$ NTs\[12\]. Those studies have indicated that the current sacrificial templates are still unsatisfied and novel method should be developed for synthesis of SiO$_2$ NTs.

Coaxial electrospinning is one of the novel electrospinning techniques and allows for the manipulation of two separate solutions within one coaxial needle to produce core-sheath NFs\[13-15\]. The unique core-sheath feature of coaxial electrosprun NFs enable them a variety of applications such as energy storage\[13\], heat storage\[14\] and sustained drug delivery\[15\]. Recently, few studies have found that NTs could be easily obtained through removal of the core-part in the coaxial electrosprun NFs. For example, Dror et al. synthesized tubular polymers with an inner diameter of around 3 µm through co-electrospinning of core and shell polymeric solution\[16\]. Zhang et al. synthesized TiO$_2$ hollow NFs by co-axial electrospinning\[17\]. Inspired by those studies, it is highly expected that SiO$_2$ NTs might be also synthesized through removal of core-part from coaxial electrosprun NFs with SiO$_2$-containing sheath layer. Compared with the conventional sacrificial template-sol-gel route, coaxial electrospinning effectively avoid the deposition of SiO$_2$ layer on the surface of sacrificial template. Therefore, it is highly expected that coaxial electrosprinning could be utilized for synthesis of SiO$_2$ NTs. However, currently, little studies have addressed the synthesis of SiO$_2$ NTs by means of the coaxial electrospinning.

On those above, in this study, SiO$_2$ NTs were facilely synthesized via a coaxial electrospinning method. The core-sheath paraffin@PVP-SiO$_2$ NF films were firstly prepared through coaxial electrospinning of a sheath-liquid derived from tetraethoxysilane (TEOS), ethanol, polyvinyl pyrrolidone (PVP) and hydrogen chloride and a core-liquid of paraffin oil and then sintered at 600°C to remove the organic components to produce SiO$_2$ NTs.

2. Experimental

2.1. Preparation of sheath solution

A sheath solution for coaxial electrospinning was prepared from TEOS and PVP via a sol-gel process. In brief, 1 mL of TEOS, 1 mL of ethanol, and 0.2 mL of HCl (2 mol/L) were added to a 25-mL flask and kept stirring at room temperature for 1 h to produce SiO$_2$ sol-gel solution. PVP (0.72 g) was dissolved in 8 mL of ethanol held in a 25-mL flask and kept stirring at room temperature to produce PVP solution. Subsequently, SiO$_2$ sol-gel solution was added to PVP solution and the mixture was kept stirring at room temperature for 30 min to produce PVP-SiO$_2$ sol-gel mixture as sheath solution for coaxial electrospinning.

2.2. Synthesis of core-sheath electrosprun NFs

The core-sheath electrosprun NF film was fabricated via coaxial electrospinning technique. PVP-SiO$_2$ sol-gel mixture as shell-liquid was transferred to a 20-mL syringe mounted on a syringe pump, while paraffin oil as core solution was transferred to another 20-mL syringe mounted on another syringe pump. Both syringes were connected with the silicon rubber tubes to a coaxial needle with an outer diameter of 1.45 mm and an inner diameter of 0.51 mm. The distance between the coaxial needle and the collector was 15 cm. The feeding speed of both core and sheath solution was 3.5 mL/h. By applying the high voltage of 15 kV on the syringe needle, both core-liquid and shell-liquid were transferred to the coaxial electrospun paraffin@PVP-SiO$_2$ NF films which were then collected from the surface of the collector.
2.3. Synthesis of SiO₂ NTs

SiO₂ NTs were synthesized by sintering the paraffin@PVP-SiO₂ NF films at 600°C. Briefly, the as-synthesized paraffin@PVP-SiO₂ NF films were placed in the muffle furnace (KSL-1200X, Hefei Kejing Material Technology Co. Ltd., China) and sintered at 600°C for 2 h to remove the organic components and produce SiO₂ NTs.

2.4. Characterizations

Size and morphology of the as-synthesized samples were observed with a scanning electron microscope (SEM, JEOL, Japan), equipped with the energy diffractive spectrophotometer (EDS) and a transmission electron microscope (TEM, JEOL, Japan). Infrared spectra of the as-synthesized samples were measured with a Fourier transformed infrared spectroscopy (FT-IR, Bruker, Nicolet 710) with a KBr pellet method.

3. Results and discussion

A typical synthesis route for SiO₂ NTs was schematically shown in figure 1. PVP-SiO₂ sol-gel mixture as sheath layer was firstly prepared from TEOS, PVP, ethanol and HCl and then injected into the outer spinneret of the coaxial needle, while paraffin oil as core-layer was injected into the inner spinneret of the coaxial needle. By applying the high voltage between the spinneret of the coaxial needle and the Al foil-covered collector, the core-sheath paraffin@PVP-SiO₂ electrospun NF films were produced on the surface of the collector. By calcination at 600°C, the organic components were burn off from the core-sheath paraffin@PVP-SiO₂ electrospun NF films and SiO₂ NTs were produced.

![Figure 1. Schematic illustration for coaxial electrospinning synthesis of silica nanotubes.](image)

Figure 2 shows size and morphology of paraffin@PVP-SiO₂ NF films and SiO₂ NTs. The as-synthesized electrospin paraffin@PVP-SiO₂ NF films consisted of numerous NFs (figure 2a), indicating that the coaxial electrospinning was effective for synthesis of fibrous materials. However, few paraffin oils remained on the surface of the paraffin@PVP-SiO₂ NF films, which caused that some of paraffin@PVP-SiO₂ NFs looked to be fused. No any hollow cavity was observed for the individual paraffin@PVP-SiO₂ NF and each paraffin@PVP-SiO₂ NF had a solid and dense structure (figure 2b). For production of SiO₂ NTs, the paraffin@PVP-SiO₂ NF films were then calcined at 600°C. After calcination, SiO₂ NTs still maintained the fibrous structure of paraffin@PVP-SiO₂ NFs and had the similar diameter of 2320±568 nm with a shell thickness of 303±25 nm (figure 2c). The hollow structure was clearly observed for SiO₂ NTs, indicating that the calcination caused the formation of the hollow structure in SiO₂ NTs (figure 2d, arrows). To further confirm the formation of SiO₂ NTs, TEM observation was conducted for SiO₂ NTs. A sharp contrast between the central part and the edge was clearly observed due to the high electron density difference between center and edge, further confirming the formation of hollow structure in SiO₂ NTs (figure 2d, inset).
Figure 2. SEM images of paraffin@PVP-SiO$_2$ NFs (a, b) and SiO$_2$ NTs (c, d) as well as TEM image of SiO$_2$ NTs (d, inset). (Arrows indicate the hollow structure)

Figure 3. The EDS spectra of paraffin@PVP-SiO$_2$ NFs and SiO$_2$ NTs as well as FT-IR spectrum of SiO$_2$ NTs.

The EDS spectra showed that paraffin@PVP-SiO$_2$ NFs were rich in elements of C, O, and Si (figure 3a), while SiO$_2$ NTs were rich in the elements of O and Si (figure 3b). The disappearance of element C further confirmed that the sintering process indeed led to the removal of organic components and the formation of tubular structure. To further confirm the formation of SiO$_2$ NTs,
FT-IR spectrum of SiO\textsubscript{2} NTs was shown in figure 3c. A strong absorption band at 1050 cm\textsuperscript{-1} was clearly observed and normally assigned to Si-O-Si bonds, confirming the formation of SiO\textsubscript{2} NTs. In addition, no any absorption band assigned to the organic components was observed, indicating that the organic components were indeed removed during the sintering process.

The formation mechanism for SiO\textsubscript{2} NTs synthesized via the template sol-gel route has been extensively researched\cite{7-12}. A layer of SiO\textsubscript{2} was firstly established on the sacrificial templates with a subsequent removal of sacrificial templates. The formation of SiO\textsubscript{2} layer on the surface of the sacrificial template is highly dependent on the interaction between sacrificial template and silicate species. In most cases, the hydrogen bond or electric interaction between the functional groups such as –OH, –NH\textsubscript{2} and –COOH of the sacrificial templates and the silicate groups such as –Si-OH and –Si-O-Si drove off the formation of the layer of SiO\textsubscript{2}\cite{7, 12}. In the case of the present coaxial electrospinning, the coaxial electrospun NFs were firstly synthesized and then sintered to remove the organic components. The utilization of sacrificial template was completely avoided and the silicate species were encapsulated in the polymeric matrix. PVP has been extensively utilized as supportive matrix for synthesis of electrospun SiO\textsubscript{2} NF films\cite{18}. TEOS is one of the most conventional siloxane agents and rapidly hydrolyzed and condensed to produce SiO\textsubscript{2} matrix (figure 3c) under the acidic and basic condition\cite{7}. The hydrogen bonding between PVP and SiO\textsubscript{2} well supported the formation of sheath layer of PVP-SiO\textsubscript{2} in the core-sheath paraffin@PVP-SiO\textsubscript{2} NFs (figure 4). By sintering, PVP was completely removed and SiO\textsubscript{2} NTs were produced.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Possible formation mechanism of paraffin@PVP-SiO\textsubscript{2} NTs and SiO\textsubscript{2} NTs.}
\end{figure}

4. Conclusions
In summary, SiO\textsubscript{2} NTs were facilely synthesized from PVP, ethanol, HCl and TEOS via a coaxial electrospinning method. The resultant SiO\textsubscript{2} NTs exhibited the hollow tubular structure and had the diameter of 2320±568 nm.

Acknowledgements
This work was conducted with the financial support from the Shanxi Scholarship Council of China (Grant No. 2016-024).

References
[1] Pang, Y., Lim, S., Ong, H., Chong, W. (2014) A critical review on the recent progress of synthesizing techniques and fabrication of TiO\textsubscript{2}-based nanotubes photocatalysts. Appl. Catal. A-Gen., 481: 127–142.

[2] Li, Z., Branco de Barros, A., Soares, D., Moss, S., Alisaraie, L. (2017) Functionalized single-walled carbon nanotubes: cellular uptake, biodistribution and applications in drug delivery. Int. J. Pharmaceut., 524: 41–54.
[3] Lai, M., Jin, Z., Qiao, W. (2017) Surface immobilization of gelatin onto TiO₂ nanotubes to modulate osteoblast behavior. Colloid. Surface. B, 159: 743–749.

[4] Tian, M., Long, Y., Xu, D., Wei, S., Dong, Z. (2018) Hollow mesoporous silica nanotubes modified with palladium nanoparticles for environmental catalytic applications. J. Colloid Interf. Sci., 521: 132–140.

[5] Ding, H., Shao, L., Liu, R., Xiao, Q., Chen, J. (2005) Silica nanotubes for lysozyme immobilization. J. Colloid Interf. Sci., 290: 102–106.

[6] Bagheri, E., Ansari, L., Abnous, K., Taghdisi, S., Charbgoo, F., Ramezani M., Alibolandi, M. (2018) Silica based hybrid materials for drug delivery and bioimaging. J. Control. Release, 277: 57–76.

[7] Chen, S., Osaka, A., Hanagata, N. (2011) Collagen-templated sol–gel fabrication, microstructure, in vitro apatite deposition, and osteoblastic cell MC3T3-E1 compatibility of novel silica nanotube compacts. J. Mater. Chem., 21: 4332–4338.

[8] Yang, X., Tang, H., Cao, K., Song, H., Sheng, W., Wu, Q. (2011) Templated-assisted one-dimensional silica nanotubes: synthesis and applications. J. Mater. Chem., 21: 6122–6135.

[9] Kim, M., Hong, J., Lee, J., Hong, C., Shim, S. (2008) Fabrication of silica nanotubes using silica coated multi-walled carbon nanotubes as the template. J. Colloid Interf. Sci., 322: 321–326.

[10] Xiao, Q., Tao, X., Zhang, J., Chen, J. (2006) Hollow silica nanotubes for immobilization of penicillin G acylase enzyme. J. Mol. Catal. B-Enzym., 42: 14–19.

[11] Shirosaki, Y., Yoshihara, H., Chen, S., Blevins, M., Nakamura, Y., Hanagata, N., Hayakawa, S., Stamboulis, A., Osaka, A. (2012) Electrospun poly(vinyl alcohol) as a template of silica hollow and solid micro-fibrous mats. J. Ceram. Soc. Jpn., 120: 520–524.

[12] Guo, L., Wang, T., Jia, L., Chen, S., Huang, D., Chen, W. (2017) Synthesis and drug delivery property of silica nanotubes prepared using gelatin nanofibers as novel sacrificed template. Mater. Lett., 209: 334–337.

[13] Ji, L., Lin, Z., Medford, A.J., Zhang, X. (2009) Porous carbon nanofibers from electrospun polyacrylonitrile/SiO₂ composites as an energy storage material. Carbon, 47: 3346–3354.

[14] Noyan, E., Onder, E., Sarier, N., Arat, R. (2018) Development of heat storing poly(acrylonitrile) nanofibers by coaxial electrospinning. Thermochim. Acta, 662: 135–148.

[15] Lu, Y., Huang, J., Yu, G., Cardenas, R., Wei, S., Wujcik, E., Guo, Z. (2016) Coaxial electrospun fibers: applications in drug delivery and tissue engineering. WIREs Nanomed. Nanobi., 8: 654–677.

[16] Dror, Y., Salalha, W., Avrahami, R., Zussman, E., Yarin, A.L., Dersch, R., Greiner, A., Wendorff, J.H. (2007) One-step production of polymeric microtubes by co-electrospinning. Small, 3: 1064–1073.

[17] Zhang, X., Thavasi, V., Mhaisalkar, S.G., Ramakrishna, S. (2012) Novel hollow mesoporous 1D TiO₂ nanofibers as photovoltaic and photocatalytic materials. Nanoscale, 4: 1707–1716.

[18] Roh, S.H., Lee, Y.A., Lee, J.W., Kim, S.I. (2008) Preparation and characterization of electrospun silica nanofibers from PVP/P123 blended polymer solution. J. Nanosci. Nanotechnol., 8: 5147–5151.

[19] Chen, S., Zhang, Q., Jia, L., Du, X., Hanagata, N. (2015) A facilely controlled length, cytotoxicity, length-dependent and cell type-dependent cellular uptake of silica nanotubes and their applications in the delivery of immunostimulatory CpG oligodeoxynucleotides. J. Mater. Chem. B, 3: 7246–7254.