

Synthesis of SiO₂/SnO₂ nanofibers using TEMPO-oxidized cellulose nanofibers as templates

Shunsuke Gunji*, Yasuhiko Shimotsuma*, Tetsuya Fujimoto and Kiyotaka Miura

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan

Abstract

SiO₂/SnO₂ nanofibers were synthesized using templates of TEMPO-oxidized cellulose nanofibers (TOCN). SiO₂ and SnO₂ were sequentially deposited onto the TOCN via sol-gel reactions. Acetylacetone (acac) and NH₃ were used to stabilize the precursor of SnO₂ through the formation of tin acetylacetonate. After the combustion of TOCN templates, SiO₂/SnO₂ nanofibers which were composed of amorphous SiO₂ and rutile phase SnO₂ nanocrystals were obtained. Especially with the acac/Sn molar ratio of 500 under the use of NH₃, the SiO₂/SnO₂ nanofibers with the fine structure derived from TOCN templates were formed. They showed a very small diameter of around 8 nm and a high specific surface area of 322 m²/g. The SnO₂ crystallite size was kept to be 3.2 nm by suppressing the coarsening. We have also evaluated the gas-sensitivity to 1000 ppm ethanol of the synthesized SiO₂/SnO₂ nanofibers. By adding acac under the use of NH₃ leading to the suppression of the growth of the SnO₂ crystallite size, this sensitivity was enhanced 10 times larger.

Introduction

Nanofibers have remarkable properties of high mechanical strength, high specific surface area, hydrodynamic characteristics, and electrical conductivities [1-4]. Especially, semiconducting metal oxide nanofibers, such as SnO₂ nanofibers, are expected to be one of key materials for gas sensing devices due to their unique electrical features [5]. Although nanofibers are conventionally produced by several ways, such as electrospinning, it is difficult to synthesize nanofibers with a diameter of ten nanometers or less [6-8]. According to the various reports on the fabricating inorganic nanofibers using the templates of cellulose nanofibers [9-12], the advantages of these procedures are basically to obtain inorganic nanofibers maintaining the fine structure corresponding to the original cellulose. More recently, we developed the method to synthesize very thin SiO₂/TiO₂ core-shell nanofibers with a diameter below ten nanometers [13] using the special cellulose nanofibers which are called (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO) oxidized cellulose nanofibers (TOCN) [14]. In this synthesis method, initially deposited SiO₂ helps TiO₂ to attach onto the cellulose nanofiber via a covalent bonding. Here, we report the synthesis of SiO₂/SnO₂ composite nanofibers by using TOCN. In the synthesis procedure, SiO₂ and SnO₂ were sequentially deposited onto the surface of TOCN. And then, the templates TOCN were combusted to obtain SiO₂/SnO₂ nanofibers. Firstly, the deposition of SiO₂ was performed via the series treatment of 3-aminopropyltrimethoxysilane (APTMS) and tetramethoxysilane (TMOS). Subsequently, SnO₂ was deposited using tin (IV) tetraisopropoxide with acac as stabilizing agent [15,16]. It is well-known that the smaller crystallite size of SnO₂ enhances its gas sensitivity [17]. In order to obtain the SiO₂/SnO₂ nanofibers with the enhanced sensitivity, the optimization of the acac/Sn molar ratio for the suppression of SnO₂ crystallites size was investigated.

Materials and methods

Preparation of TEMPO-oxidized cellulose nanofibers (TOCN)

TOCN were prepared by the conventional method [18]. 4.00 g of fibrous cellulose (KY-100G, Daicel Fine Chem) was suspended in 400 mL of distilled water. 400 mg of NaBr (Kishida Chemicals), 64.0 mg of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, Sigma-Aldrich), and 12.4 mL of NaClO solution (Wako Pure Chemicals), were added and stirred for 2.5 hours at room temperature maintaining pH value of 10. The obtained TOCN were repeatedly washed with distilled water and stored as an aqueous dispersion for further experiments.

SiO₂ deposition on TOCN

The series treatments of two types of silicon alkoxide were used [13]. Firstly, 0.98 mL of 3-aminopropyltrimethoxysilane (APTMS, Sigma-Aldrich) was added to 100 mL of 1.0wt% aqueous suspension of TOCN and stirred for 45 min at room temperature. After the stirring, the TOCN treated with APTMS were repeatedly washed with distilled water using centrifugation and were prepared to be 1.0wt% aqueous

Correspondence to: Shunsuke Gunji, Master of Engineering, Ph.D. Student, Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan, Tel: +81-75-383-2463, Fax: +81-75-383-2461

Yasuhiko Shimotsuma, Ph.D. in Engineering, Associate Professor, Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan; Tel: +81-75-383-2459, Fax: +81-75-383-2461

Key words: nanofibers, sol-gel, SiO₂, SnO₂, cellulose nanofibers, gas sensor

Received: January 08, 2017; **Accepted:** January 23, 2017; **Published:** January 26, 2017

suspension. Subsequently, 0.10 mL of tetramethoxysilane (TMOS, Sigma-Aldrich) was added to the suspension and stirred for 45 min at room temperature. The TOCN sequentially treated with APTMS and TMOS (in the following, TOCN/SiO₂) were repeatedly washed with distilled water. After that, the solvent was substituted with ethanol (Kishida Chemicals).

Synthesis of SiO₂/SnO₂ nanofibers

To deposit SnO₂ onto the TOCN/SiO₂ surface, the hydrolysis and condensation reactions of tin alkoxide were employed. Certain amount of acetylacetonate (acac, Kishida Chemicals), 3.06 mL of 28% NH₃ aqueous solution (Kishida Chemicals) were added to ethanol dispersion containing 0.128 g of TOCN/SiO₂. After the further dilution with ethanol and addition of 0.928 mL of 10w/v% tin (IV) isopropoxide in isopropanol (Alfa Aesar), the mixture was stirred for 12 h at room temperature under an argon atmosphere. In the exceptional cases, distilled water was used instead of NH₃ aqueous solution with maintaining the total amount of water. The amount of ethanol for the dilution was modified to make the total weight of the mixture 128 g. Acac/Sn molar ratios were changed from 0 to 1000. After washing repeatedly by isopropanol (Kishida Chemicals) using centrifugation at 4000 rpm, TOCN/SiO₂ covered with SnO₂ were dried with a super critical dryer (SCRD 4, Rexam) using CO₂. SiO₂/SnO₂ nanofibers were obtained after the calcination of the dried sample at 500°C for 4 h in air via the combustion of the templates TOCN.

Characterization

Measurements of X-Ray diffraction (XRD) patterns were carried out by an X-Ray diffractometer (RINT-2500HFK, Rigaku). The crystallite size of SnO₂ was calculated by Scherrer's equation with rutile SnO₂ (101) peak. Observations of microscopic structures were conducted by a field-emission scanning electron microscope (FE-SEM; JSM-6700F, JEOL) and a transmission electron microscope (TEM; JEM-2200FS, JEOL). FT-IR spectra were measured by an FT-IR spectrometer equipped with an ATR accessory (Spectrum Two, Perkin Elmer). Specific surface areas were determined by using an N₂ adsorption-desorption apparatus (Tristar 3000, Shimadzu) after degassing at 150°C.

Evaluation of gas sensitivity

The gas sensitivity of the synthesized SiO₂/SnO₂ nanofibers was evaluated by monitoring changes of an electrical resistance of the nanofibers during repeated exposure to the analyte gas containing ethanol. SiO₂/SnO₂ nanofibers were formed to be a sheet with a size and a thickness of about 8 mm × 13 mm and 1 mm, respectively. The gold electrode was deposited on the sheet by sputtering. The nanofibers sheet was placed on a ceramic heater inside a silica glass tube and the measurements were conducted at 400°C. The analyte gas containing 1000 ppm ethanol with the flow rate of 300 sccm was prepared by using the mass flow controllers (SEC-E40, Horiba Tec).

Results and discussion

Figure 1 shows the synthesis procedure of the SiO₂/SnO₂ nanofibers schematically.

Figure 2 shows XRD patterns of SiO₂ and SiO₂/SnO₂ nanofibers synthesized with various acac/Sn molar ratios. All SiO₂/SnO₂ nanofibers had rutile phase SnO₂ (JCPDS card no. 41-1445), in contrast to no crystalline peaks in SiO₂. Inset denotes the relationship between acac/Sn ratios and crystallite sizes. It should be noted that SiO₂/SnO₂

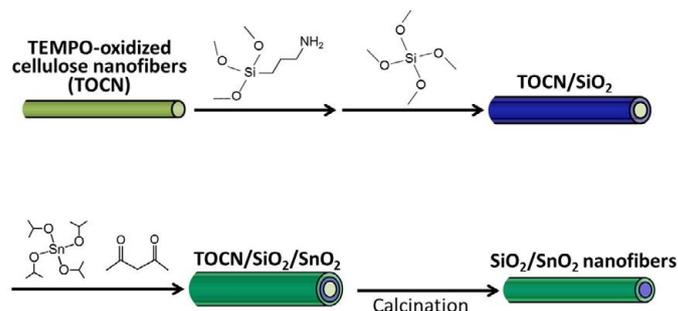


Figure 1. Schematic procedure for synthesis of SiO₂/SnO₂ nanofibers.

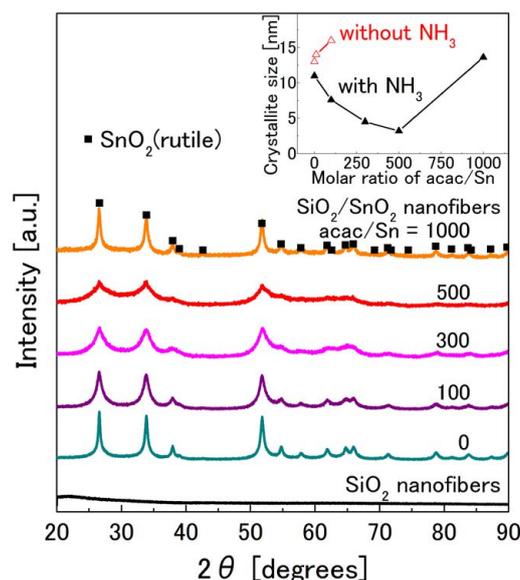


Figure 2. XRD patterns of SiO₂ and SiO₂/SnO₂ nanofibers synthesized with various acac/Sn molar ratios. Inset plot indicate relationship between acac/Sn molar ratios and crystallite size of SnO₂. Red-colored plots indicate results of SiO₂/SnO₂ nanofibers without use of NH₃, as exceptional cases.

nanofibers obtained by the acac/Sn ratio of 500 showed the smallest crystallite size of 3.2 nm. In the exceptional cases without NH₃, the crystallite sizes remained still high. Therefore, in the following, we focused on the results with the use of NH₃.

Figure 3 shows FE-SEM images of TOCN, SiO₂ nanofibers, and SiO₂/SnO₂ nanofibers with various acac/Sn ratios. The SiO₂/SnO₂ nanofibers with the acac/Sn ratio of 500 maintained the fine structure derived from TOCN, however, the others possessed considerably coarse grains. These coarsening are corresponding to the large crystallite sizes in the inset of Figure 2. From these results, it was revealed that the use of NH₃ and appropriate amount of acac can suppress the undesirable large grains. The generation of such coarse grains would be interpreted as follows; since a homogeneous nucleation via a self-condensation of tin isopropoxide occurred, these nuclei grew and then attached onto the surface of the nanofibers. Here the effect of acac can be explained by the formation of tin acetylacetonate. Such tin acetylacetonate, which is less reactive than tin alkoxide [15,16], suppressed self-condensation and finally caused the selective deposition on the nanofibers surface. In this study, since the formation of acetylacetonate occurred at the same time as the hydrolysis of tin isopropoxide, much more amount of acac compared to the stoichiometric acac/Sn molar ratio, which is up to 2, was required. It is assumed that the basicity of NH₃ helped the formation of tin acetylacetonate through the deprotonation of acac

[19]. On the other hand, it is expected that NH₃ also acted as base for the dissolution of small nuclei derived from the self-condensation. Since acac is weak acid, the too much amount as acac/Sn ratio of 1000 caused the insufficiency of basicity for the dissolution of nuclei derived from the self-condensation, leading to the coarsening of SnO₂ crystallites. It should be emphasized that a smaller crystallite size is desirable for a more sensitive gas sensor [17]. By TEM observation (Figure 3F-H), SiO₂/SnO₂ nanofibers with the acac/Sn ratio of 500 had the diameter of around 8 nm. They were covered with rutile SnO₂ nanocrystals (Figure 3G, H). It can be interpreted that SiO₂/SnO₂ nanofibers have the core/shell structure reflecting the sequential deposition of SiO₂ and SnO₂ [13].

Furthermore, they exhibited an enormously high specific surface area of 322 m²/g (Table 1). The IR spectrum of SiO₂/SnO₂ nanofibers with the acac/Sn ratio of 500 was compared to that of the SiO₂ nanofibers (Figure 4). Typical amorphous SiO₂ peaks, such as Si-O-Si asymmetric stretching modes around 1250 cm⁻¹ and 1080 cm⁻¹ [20], were observed in both samples. In the case of the SiO₂/SnO₂ nanofibers, the peak at around 970 cm⁻¹ and the broad peak between 700 and 400 cm⁻¹ are assigned to Si-O-Sn stretching mode and typical SnO₂ absorption, respectively [21,22]. Due to the presence of Si-O-Sn peak, this result can be interpreted by the existence of the covalent bonding between SnO₂ and SiO₂.

Figure 5 shows the resistance changes of the SiO₂/SnO₂ nanofibers with the different synthesis conditions under the cyclic exposure to the analyte gas containing 1000 ppm ethanol. The gas sensitivity is defined as the ratio of the resistance before and after the exposure to an analyte gas [17]. The relationships between the crystallite sizes and sensitivities for the synthesized SiO₂/SnO₂ nanofibers were shown in Table 1. The SiO₂/SnO₂ nanofibers with the acac/Sn ratio of 500 exhibited the simply high sensitivity value of 228 which is about 10 times as high as that with the acac/Sn of 0. It can be interpreted in terms of their smaller crystallite size [17].

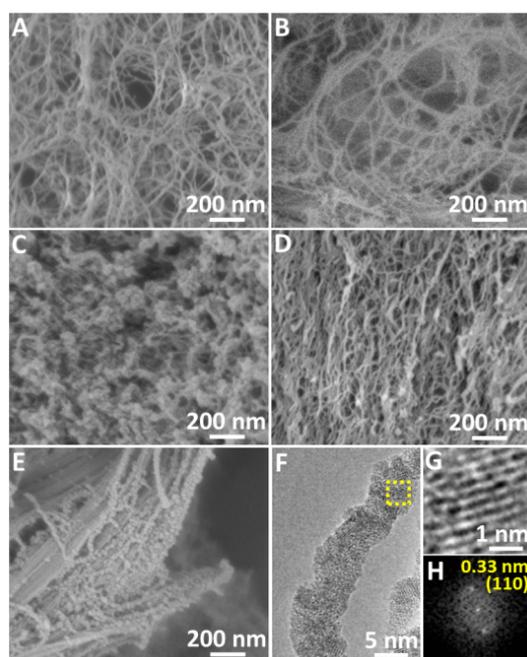


Figure 3. FE-SEM images of (A) TOCN, (B) SiO₂ nanofibers, (C)-(E) SiO₂/SnO₂ nanofibers synthesized with acac/Sn molar ratio of 0, 500, 1000, respectively. TEM image of (F) SiO₂/SnO₂ nanofibers synthesized with acac/Sn molar ratio of 500, (G) high magnified image of selected area in (F). FFT image of (F) is shown in (H).

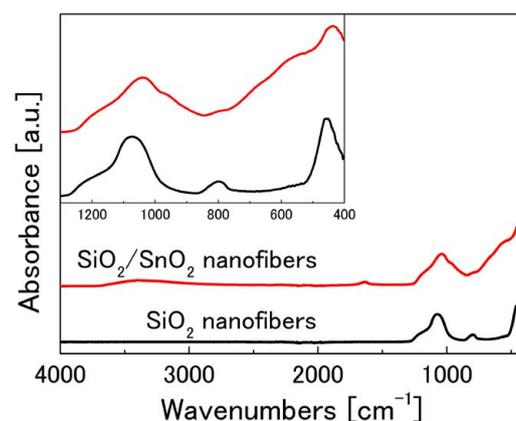


Figure 4. FT-IR spectra of SiO₂ nanofibers and SiO₂/SnO₂ nanofibers synthesized with acac/Sn molar ratio of 500.

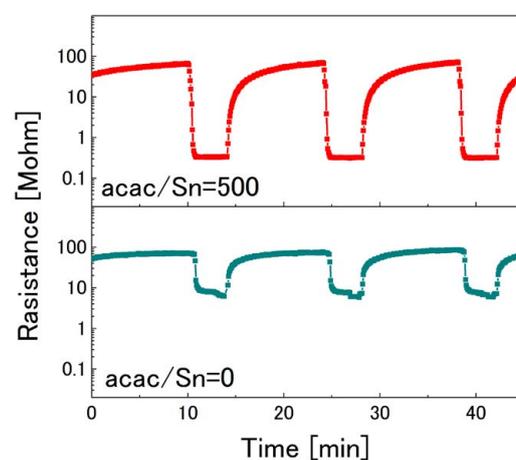


Figure 5. Repetitive responses to 1000 ppm ethanol gas at 400°C.

Conclusion

We successfully synthesized SiO₂/SnO₂ nanofibers using TEMPO-oxidized cellulose nanofibers (TOCN) as templates. To obtain SiO₂/SnO₂ nanofibers, the templates of TOCN were combusted after the sequential deposition of SiO₂ and SnO₂ onto the surface of TOCN. SiO₂/SnO₂ were composed of amorphous SiO₂ and rutile phase SnO₂ nanocrystals. The detailed crystalline and microscopic structures were investigated in relation to the deposition condition of SnO₂. The key factor was the molar ratio of acac/Sn and the presence of NH₃. The optimal molar ratio of acac/Sn was 500 under the use of NH₃. Since such optimized SiO₂/SnO₂ nanofibers keep the fine structure derived from TOCN, it can be expected that the crystallite size is controllable. Indeed, the synthesized nanofibers had a very thin diameter of around 8 nm and the smallest crystallite size of rutile SnO₂ of 3.2 nm. We have also demonstrated that these nanofibers exhibited the high gas sensitivity of 228 to 1000 ppm ethanol, which is derived from the small crystallite size of SnO₂. The synthesized SiO₂/SnO₂ nanofibers are also expected to exhibit high gas sensitivity to other volatile organic compounds (VOC). More detailed investigations are required.

Acknowledgements

This work was partially supported by JSPS KAKENHI Grant Number 16K13929, The Thermal & Electric Energy Technology Foundation, Tokuyama Science Foundation, Cross-Ministerial

Strategic Innovation Promotion (SIP) Program, and Nanotechnology Platform Program of MEXT, JAPAN.

References

- Chen F, Peng X, Li T, Chen S, Wu XF, Reneker HR, Houl H (2008) Mechanical characterization of single high-strength electrospun polyimide nanofibers. *Journal of Physics D: Applied Physics* 41: 025308.
- Thavasi V, Singh G, Ramakrishna S (2008) Electrospun nanofibers in energy and environmental applications. *Energy & Environmental Science* 1: 205.
- Aronggaowa B, Toda Y, Ito N, Shikinaka K, Shimomura T (2013) Transparent conductive films fabricated from polythiophene nanofibers composited with conventional polymers. *Polymers* 5: 1325.
- Shen S, Henry A, Tong J, Zheng R, Chen G (2010) Polyethylene nanofibres with very high thermal conductivities. *Nat Nanotechnol* 5: 251-255. [[crossref](#)]
- Arafat MM, Dinan B, Akbar SA, Haseeb AS (2012) Gas sensors based on one dimensional nanostructured metal-oxides: a review. *Sensors (Basel)* 12: 7207-7258. [[crossref](#)]
- Kim I-D, Rothschild A (2011) Nanostructured metal oxide gas sensors prepared by electrospinning. *Polymers for Advanced Technologies* 22: 318.
- Li D, Xia Y (2004) Electrospinning of nanofibers: reinventing the wheel? *Advanced Materials* 16: 1151.
- Holmström SC, King PJS, Ryadnov MG, Butler MF, Mann S, Woolfson DN (2008) Templating silica nanostructures on rationally designed self-assembled peptide fibers. *Langmuir* 24: 11778.
- Gu Y, Huang J (2013) Precise size control over ultrafine rutile titania nanocrystallites in hierarchical nanotubular silica/titania hybrids with efficient photocatalytic activity. *Chemistry - A European Journal* 19: 10971.
- Zhang Y, Liu X, Huang J (2011) Hierarchical mesoporous silica nanotubes derived from natural cellulose substance. *ACS Applied Materials & Interfaces* 3: 3272.
- Korhonen JT, Hiekkataipale P, Malm J, Karppinen M, Ikkala O, et al. (2011) Inorganic hollow nanotube aerogels by atomic layer deposition onto native nanocellulose templates. *ACS Nano* 5: 1967-1974. [[crossref](#)]
- Huang J, Matsunaga N, Shimano K, Yamazoe N, Kunitake T (2005) Nanotubular SnO₂ templated by cellulose fibers: synthesis and gas sensing. *Chemistry of Materials* 17: 3513.
- Gunji S, Shimotsuna Y, Miura K (2016) Synthesis and photocatalytic properties of SiO₂/TiO₂ nanofibers using templates of TEMPO-oxidized cellulose nanofibers. *Journal of Sol-Gel Science and Technology* 79: 151.
- Isogai A, Saito T, Fukuzumi H (2011) TEMPO-oxidized cellulose nanofibers. *Nanoscale* 3: 71-85. [[crossref](#)]
- Hampden-Smith MJ, Wark TA, Brinker CJ (1992) The solid state and solution structures of tin(IV) alkoxide compounds and their use as precursors to form tin oxide ceramics via sol-gel-type hydrolysis and condensation. *Coordination Chemistry Reviews* 112: 81.
- Briois V, Belin S, Chalaça MZ, Santos RHA, Santilli CV, Pulcinelli S (2004) Solid-state and solution structural study of acetylacetonate-modified Tin(IV) chloride used as a precursor of SnO₂ nanoparticles prepared by a sol-gel route. *Chemistry of Materials* 16: 3885.
- Xu C, Tamaki H, Miura N, Yamazoe N (1991) Grain size effects on gas sensitivity of porous SnO₂-based elements. *Sensors and Actuators B: Chemical* 3: 147.
- Saito T, Kimura S, Nishiyama Y, Isogai A (2007) Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose. *Biomacromolecules* 8: 2485.
- Seco M (1989) Acetylacetonate: a versatile ligand. *Journal of Chemical Education* 66: 779.
- Wang J, Zou B, El-Sayed MA, (1999) Comparison between the polarized Fourier-transform infrared spectra of aged porous silicon and amorphous silicon dioxide films on Si (100) surface. *Journal of Molecular Structure* 508: 87.
- Shah P, Ramaswamy AV, Lazar K, Ramaswamy V (2004) Synthesis and characterization of tin oxide-modified mesoporous SBA-15 molecular sieves and catalytic activity in trans-esterification reaction. *Applied Catalysis A: General* 273: 239.
- Amalric-Popescu D, Bozon-Verduraz F (2001) Infrared studies on SnO₂ and Pd/SnO₂. *Catalysis Today* 70: 139.

Copyright: ©2017 Gunji S. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.