DOI 10.5162/sensor2013/B4.4

Mesoporous Al-doped SnO_2 nanotubes with enhanced gas-sensing properties fabricated by electrospinning

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Abstract

Fabrication of metal-oxide nanotubes with quasi-one dimensional (Q1D) nanostructure is complex and expensive. In this work, mesoporous Al-doped SnO_2 nanotubes were fabricated by a facile route of simple electrospinning. SEM and HRTEM characterizations of these nanotubes exhibited distinctive mesoporous hollow Q1D structure with 150 nm inner diameter and 250 nm outer diameter. The gas-sensing properties of the nanotubes with varying Al/Sn ratio were tested under variable temperature and formaldehyde (HCHO) concentration. At first, the gas-sensing response increased with the rise of Al amount and reached the maximum response value with the Al/(Al+Sn) ratio of 8:100. Then the response decreased with further increasing Al ratio in SnO_2 nanotubes. The results indicated the novel application of electrospinning fabricated metal-oxide semiconductor nanotubes in gas-sensing field, and point towards a promising approach for improving gas response of electrospun materials.

Key words: nanotubes, electrospinning, mesoporous, gas-sensing properties

1. Introduction

One dimensional (1D) and quasi-one dimensional (Q1D) nanostructures (nanowires, nanorods, nanobelts, nanotubes and so on) attracts global attention because of their unique structures, electrical, electrochemical, and catalytic properties which are closely related to its high surface-to-volume ratio [1][2]. Nanotube attracts intensive research motivation, and is widely applied in chemical gas sensors [3], dye sensitized solar cells [4], photocatalysts [5] and biomolecular devices [6]. The main synthesis approaches to date for nanotubes have been anodic oxidation to produce metal oxide [7], and chemical or physical deposition on sacrificial templates [8]. Comparing with these approaches, electrospinning offers several advantages just like low cost, easy fabrication, tunable process parameters [9]. Despite the gradually increasing research activities in electrospinning, the application of electrospun nanotubes in gas-sensing field is rarely seen in the literatures.

Al is one of the most frequent chemical elements and widely applied in material preparation. Al is used as effective dopant for SnO_2 in field emission [10], photoluminescence [11], electrochemical [12], however, there are

few reports focus on relationship between the amount of Al in SnO_2 and consequently gas-sensing properties. Therefore, there is of great significant to explore the influence of Al on gas-sensing properties of SnO_2 nanotubes.

In this work we present a new strategy for the fabrication of unique nanotubes, assembled by fine SnO_2 particles, with typical Q1D nanostructure. The gas-sensing properties of Al doped SnO_2 nanotubes are investigated, the test results reveals that at first the rise up of Al amount in SnO_2 leads to the increasing gas-sensing response, until the Al/(Al+Sn) ratio reaches 8:100. Then the further increasing Al amount results in a drastic decreasing in gas-sensing response. The results indicate great potential of electrospinning fabricated metal-oxide-semiconductive nanotubes in gas-sensing application.

2. Experimental

2.1 Preparation of SnO_2 nanotubes

Ethanol, N,N-dimethyl formamide (DMF), $SnCl_2{\cdot}2H_2O$ and $AlCl_3{\cdot}6H_2O$ were purchased from Shanghai Chemical Corp., . Poly (vinyl pyrrolidone) (PVP, Mw≈1,300,000) was purchased from Aldrich. All chemicals were the analytical-grade reagents and used as received without any further purification. 1 g PVD, 4.5 g DMF and 4.5 g ethanol were mixed together, following by vigorous stirring for 6 h at room temperature. Then 1 g $SnCl_2{\cdot}2H_2O$ and a certain amount $AlCl_3{\cdot}6H_20$ of were added into the mixture by the molar ratio of Al/(Al+Sn) (0:100, 4:100, 6:100, 8:100, 10:100, 12:100). The mixture was stirred for 1 h and then was added into a 20 ml plastic syringe with a stainless steel needle. The precursor fibers were obtained by electrospinning with a collection distance of 15 cm between the needle and the flat collector and an voltage of 10 kV was applied on the needle. The obtained electrospinning fibers were dried for 12 h at 80 °C. Calcination (heating rate was 2 °C·min^{-1}, 600 °C for 2 h in an oven) was performed to remove the organic constituents of PVP and crystallize the SnO_2. Then the nanotubes were obtained. The calcined fiber with Al/(Al+Sn) molar ratio for 4:100, 6:100, 8:100, 10:100, 12:100, were denoted as 4Al-SnO_2, 6Al-SnO_2, 8Al-SnO_2, 10Al-SnO_2 and 12Al-SnO_2, respectively.

2.2 measurements

The calcined fibers and a certain amount of ethanol were mixed to form paste. Then the paste was coated on the surface of an alumina ceramic tube, which have two Au electrodes and Pt wires at both electrodes. The coated ceramic tubes were sintered at 500 °C for 2 h. A small heating wire of Ni-Cr alloy was inserted through the ceramic tube when the ceramic tube was fixed on a 6-stitches substrate. In order to improve the long-term stability, the sensor devices were aged at 320 °C for 5 days in air.

The gas-sensing properties were tested in a steel-made chamber through which a controlled atmosphere was allowed to flow. The electrical response of the sensor was measured with an automatic test system, controlled by personal computer. The gas-sensing properties were assessed by sensor response, S, as the resistance ratio R_a/R_g, where R_a and R_g stood for the electrical resistance in dry air and in the tested gas, respectively. In this paper, the gas sensitivity of the sensors was measured for low concentration HCHO.

3. Results and discussion

3.1 Structure and morphology of SnO_2 nanotubes

The images of (a) and (b) of Fig. 1. show the SEM images of the as-spun fibers and the calcined nanotubes of 8Al-SnO_2. As exhibited in Fig. 1a, the uniform, smooth, and long continuous composite fibers are formed. The average diameter of as-spun fibers is 300 nm.

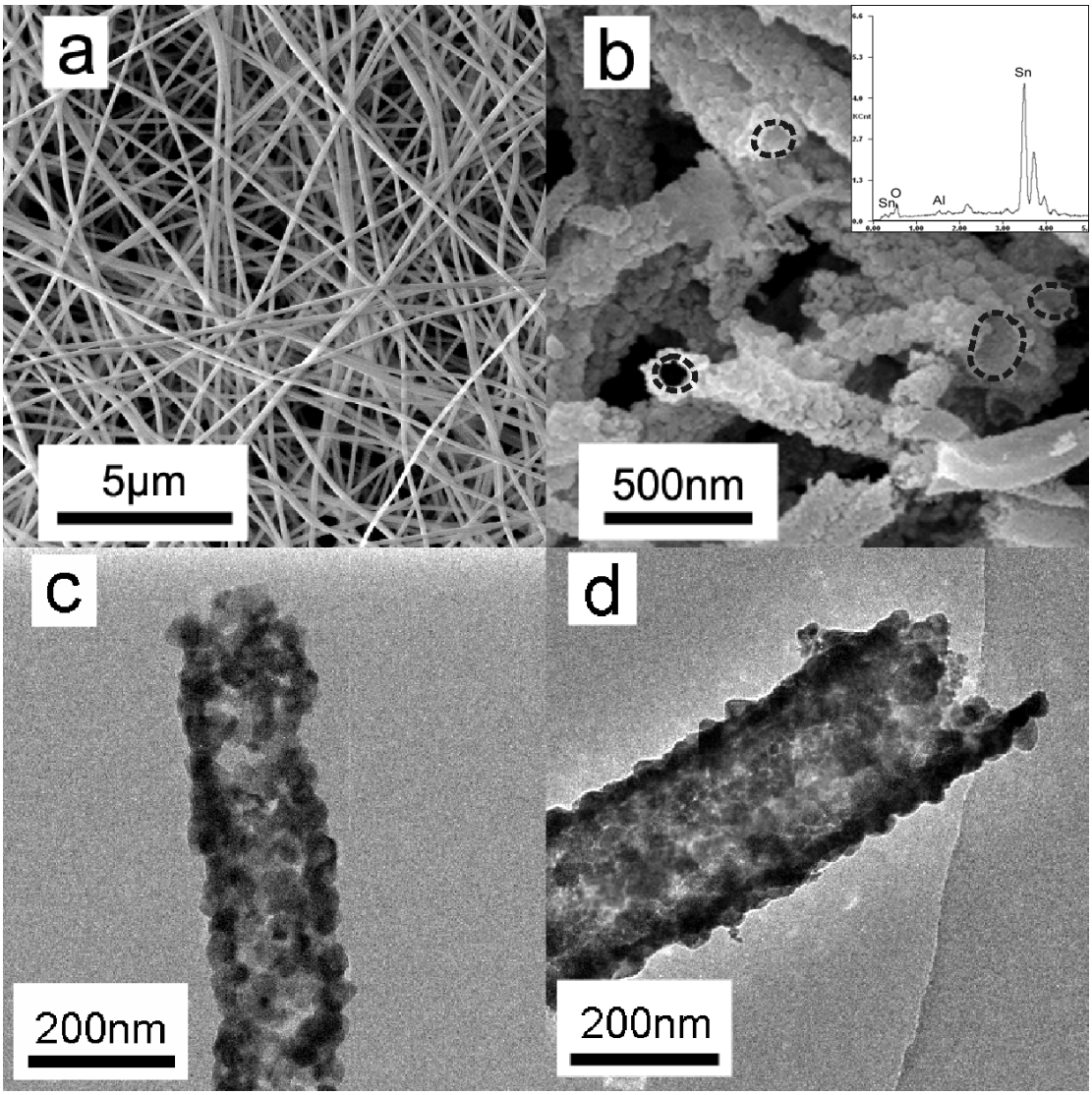

Fig. 1. (a) As-spun fibers and (b) their nanotubes obtained from calcination. (c) and (d) are TEM images of pure SnO_2 and 8Al-SnO_2.

After the calcination at 600 °C, SnO_2 nanotubes are obtained, as shown in Fig. 1b. The nanotubes are assembled by fine crystalline SnO_2 with 150 nm inner diameter and 250 nm outer diameter. EDX has been used to prove the existence of Al component in SnO_2 nanotubes, and the spectra is illustrated in the inset of Fig. 1b. From the EDX pattern, the Al peak can be detected confirming the existence of Al component in the nanotubes. The images of (c) and (d) of Fig. 1. are the TEM images of calcined nanotubes of pure SnO_2 and 8Al-SnO_2, and the diameters of these two samples is about 200 nm and 250 nm, respectively. Comparing with the as-spun fibers, the out diameters of calcined nanotubes show slight shrinkage. The particle diameter of pure SnO_2 nanotubes is 15 nm, which is nearly the same with 8Al-SnO_2, as observed in the TEM images.

The structures of the as-spun fibers and nanotubes formed during calcination are characterized by XRD, as shown in Fig. 2. As seen from the XRD spectra, the as-spun fibers exhibits no inorganic diffraction peaks. With the calcination process, all the samples show intensive diffraction peaks, and All the peaks, (110), (101), (201) and so on, agree well with the tetragonal structure in JCPDS 41-1445 (cassiterite), it indicates that the materials are

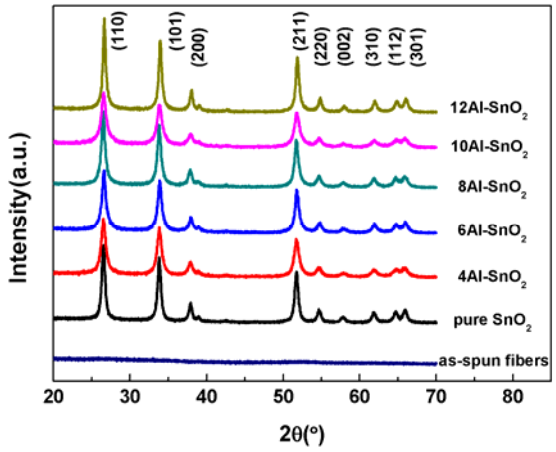

Fig. 2. XRD spectra of as-spun fibers and pure SnO_2 and SnO_2 nanotubes with varing Al/Sn molar ratio.

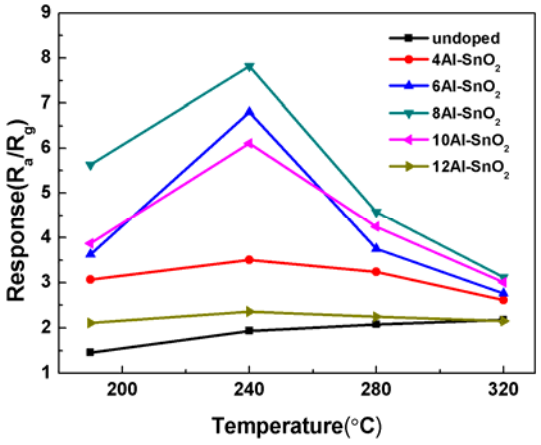

Fig. 3. Sensitivity dependence of operation temperature to 1ppm HCHO.

consist of tetragonal SnO_2. No peaks of impurities are observed from these patterns. Average crystallinity sizes of the nanotubes are about 16nm, this result agrees well with the observed results in TEM images.

3.2 The gas-sensing properties

Fig. 3 shows the dependence of the sensor response on working temperature to 1ppm HCHO. It can be observed that the pure SnO_2 nanotubes show low response to HCHO, the sensitivity is less than 2 to 1ppm HCHO at 240°C. Except for pure SnO_2, the gas-sensing response of all the samples increase with the increasing operation time and the sensitivities get the maximum value at 240 °C, indicating that the optimal operation temperature of Al doped SnO_2 nanotubes is 240 °C. Additionally, the gas-sensing response to 1ppm HCHO rises up with the increase of Al molar ratio in the SnO_2 nanotubes, and gets the maximum value when the molar ratio is 8%. Then it goes down when the Al molar ratio continues to increase. The gas-sensing response of 8% nanotubes to 1ppm HCHO is about 8 at 240 °C, it indicated that the sensitivity increases with the rise up of Al molar ration in SnO_2 until Al/(Al+Sn) reaches 8%. Therefore, the optimal Al amount doping in SnO_2 is 8%, then the increasing Al amount

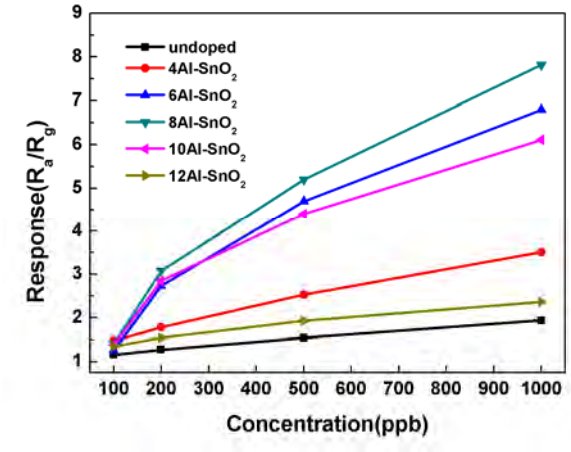

Fig. 4. Sensitivity dependence of HCHO concentration at 240°C.

causes excessive doping, which would result in lower gas-sensing sensitivity.

Fig. 4 shows the dependence of response of sensors fabricated by pure SnO_2 and Al doped SnO_2 nanotubes on HCHO gas concentration. The response of each sample gradually increased with the increasing concentration of HCHO gas. 8Al-SnO_2 shows the highest sensing response value to HCHO comparing with that of others.

To test the stability, 5 periods of 8Al-SnO_2 gas sensor's dynamic curve to 1ppm HCHO at 240°C are shown in Fig. 5. There is almost no change in the voltage, which directly confirm

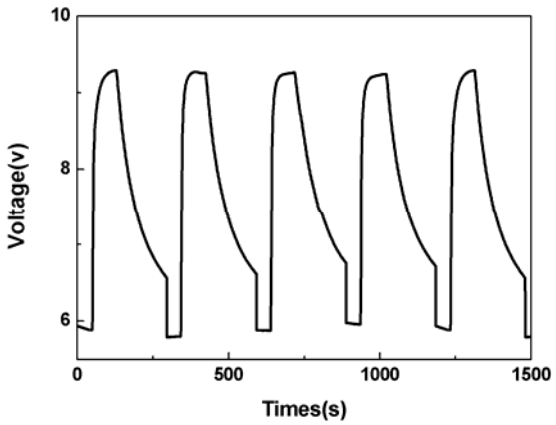

Fig. 5. Five periods of 8A gas sensors examined to 1ppm HCHO gas at 240°C.

the good stability of our sensors. The good reproducibility can be attributed to the high temperature annealing. After annealed at 600°C, the crystallization of SnO_2 fibers is complete [14]. The electrospinning produced nanotubes has great potential in gas-sensing device fabrication.

The formation mechanism of nanotubes prepared by electrospinning followed with calcinations is probably like the following process. It was suggested some primary nanoparticles were firstly formed in the precursor fibers with the removing of PVP in the annealing, in both the outside and inner sites. At a relatively lower temperature, the reaction rate on the outside was larger than that in the inner due to thermal unbalance, leading to the constriction of outside nanoparticles and formation of nanowires. At an appropriate temperature (here is 600 °C), the reaction rate in the inner sites more quickly increased. In this case, the outside particles constricted, while the inner particles expanded due to large strain strength, leading to the formation of nanotubes [15].

4. Conclusion

Al doped SnO_2 nanotubes with 150 nm inner diameter and 250 nm outer diameter are successfully prepared by facial and simple electrospinning and subsequently calcination at 600°C. The Al-SnO_2 nanotubes fabricated gas sensors exhibits variable gas-sensing response to varying HCHO concentration. The 8Al-SnO_2 shows optimal sensitivity. Except for pure SnO_2, all the samples show their optimal temperature of 240°C.

References

[1] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Gates, Y. Yin, F. Kim and H. Yan, One-Dimensional Nanostructures: Synthesis, Characterization, and Applications, *Advanced Materials* 15, 353-389 (2003); doi: 10.1002/adma.200390087.

[2] J. Lu, P. Chang, Z, Fan, Quasi-One-Dimensional Metal Oxide Materials-Synthesis, Properties and Applications, *Materials Science and Engineering R* 52, 49-91 (2006); doi: 10.1016/j.mser.2006.04.002.

[3] J. Chen, L. Xu, W. Li, X. Gou. α-Fe_2O_3 Nanotubes in Gas Sensor and Lithium-Ion Battery Applications, *Advanced Materials* 17, 582-586 (2005); doi: 10.1002/adma.200401263.

[4] B. Lei, Q. Luo, Z. Sun, D. Kuang, C. Su, Fabrication of Partially Crystalline TiO_2 Nanotube arrays using 1,2-Propanediol Electrolytes and Application in Dye-Sensitized Solar Cells, *Advanced Powder Technology* 24, 175-182 (2013); doi: 10.1016/j.apt.2012.05.005.

[5] J. A. Grasser, B. K. Stover, D. S. Muggli, Synthesis Factors that Impact TiO_2 Nanotube Activity during Gas-Phase Photocatalytic Oxidation of Methanol, *Chemical Engineering Communications* 200, 337-350 (2013); doi: 10.1080/00986445.2012.708686.

[6] F. Patolsky, G. Zheng, C. M. Lieber, Nanowire Sensors for Medicine and the Life Sciences, *Nanomedicine* 1, 51-65 (2006); doi: 10.2217/17435889.1.1.51.

[7] C. A. Grimes. Synthesis and Application of Highly Ordered Arrays of TiO_2 Nanotubes, *Journal of Materials Chemistry* 15, 1451-1457

(2007); doi: 10.1039/B701168G.
[8] J. Lu, P. Chang, Z, Fan, Quasi-One-Dimensional Metal Oxide Materials-Synthesis, *Materials Science and Engineering R* 52, 49-91 (2006); doi: 10.1016/j.mser.2006.04.002.
[9] L. Xu, B. Dong, Y. Wang, J. Chen, Q. Liu, H. Song. Porous In_2O_3: RE (RE=Gd, Td, Dy, Ho, Er, Tm, Yb) Nanotubes: Electrospinning Preparation and Room Gas-Sensing Properties, *Journal of Physical Chemistry C* 114, 9089-9095 (2010); doi: 10.1021/jp101115v.
[10] L. Ma, Y. Ye, L. Hu, K. Zheng, T. Guo. Efficient field emission from patterned Al-doped SnO_2 nanowires, *Physica E* 40, 3127-3130 (2008) ; doi: 10.1016/j.physe.2008.04.011.
[11] M. Lei, Q. Hu, S. Wang, W. Tang. Structural and optical properties of Al-doped SnO_2 nanowires, *Materials Letters* 64, 19-21 (2010); doi: 10.1016/j.matlet.2009.09.058.
[12] R. Alcantara, F. J. Fernandez-madrigal, C. Perez-Vicente. J. L. Tirado, J. C. Jumas, J. Olivier-Fourcade. Preparation, Sintering, and electrochemical Properties of Tin Dioxide and Al-Doped Tin Dioxides Obtained from Citrate Precursors, *Chemistry of Materials* 12, 3044-3051 (2000); doi: 10.1021/cm991180i.
[13] X. Ding, D. Zeng, C. Xie, Controlled Growth of SnO_2 Nanorods Clusters via Zn Doping and its Influence on Gas-sensing Properties, *Sensors and Actuators B: Chemical* 149, 336-344 (2010); doi: 10.1016/j.snb.2010.06.057.
[14] Zhang, X. He, J. Li, Z. Miao, F. Huang, Fabrication and Ethanol-Sensing Properties of Micro Gas Sensor Based on Electrospun SnO_2 Nanofibers. *Sensors and Actuators B: Chemical* 132, 67-73 (2008); doi:10.1016/j.snb.2008.01.006.
[15] L. Xu, B. Dong, Y. Wang, X. Bai, Q. Liu, H. Song, Electrospinning Preparation and Room Temperature Gas Sensing Properties of Porous In_2O_3 Nanotubes and Nanowires. *Sensors and Actuators B: Chemical* 147, 531-538 (2010): doi: 10.1016/j.snb.2010.04.003.