Key Engineering Materials Vols. 575-576 (2014) pp 45-49
Online available since 2013/Sep/04 at www.scientific.net

doi:10.4028/www.scientific.net/KEM.575-576.45

Synthesis and Oxygen Sensing Properties of $Ti_{1-x}Sn_xO_2$ Solid Solutions Nanoparticles

Aiqing Wu[1,2], Xinzuo Fang[1,2], Xinhua Lin[2], Huanqin Wang[2], Yingxian Wang[2], Rui Zhang[2], Lisheng Gao[2,*]

[1]Department of Materials Science and Engineering, University of Science and Technology of China
[2]State Key Laboratory of Transducer Technology, Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei 230031, China
* Corresponding Author: Lisheng Gao, E-mail: gls2405@ ustc.edu

Keywords: Rutile TiO_2; SnO_2; $Ti_{1-x}Sn_xO_2$ solid solution; Sol-gel process; Hydrothermal method; Oxygen sensing

Abstract: Rutile $Ti_{1-x}Sn_xO_2$ ($0.2 \leq x < 1$) solid solutions had been prepared using a sol-hydrothermal method, which combined the conventional sol-gel process with hydrothermal method. Hybrid alkoxides of Ti^{4+} and Sn^{4+} were used as precursors in the sol-gel process and Sn^{4+} served as crystal-inducing agent during the formation of rutile crystal lattice in the hydrothermal process at 200℃. The microstructures and morphologies of nanoparticles were detected with XRD and TEM. Rutile $Ti_{1-x}Sn_xO_2$ solid solutions nanoparticles with well-distributed crystallite sizes about 10nm were obtained with Sn^{4+} content above 20mol% without any high temperature calcination. The oxygen sensitivity properties of $Ti_{1-x}Sn_xO_2$ solid solutions had also been investigated. It is proved $Ti_{1-x}Sn_xO_2$ solid solutions exhibited higher oxygen responses than single TiO_2 or SnO_2. A typical sample of $Ti_{0.5}Sn_{0.5}O_2$ presented the best sensitivity is approximately 6 under 400℃.

1. Introduction

Recently, extensive investigations have been focused on mixed metal oxides and solid solutions to seek for performances superior to single oxides [1,2]. As reported, Al_2O_3 and CeO_2–ZrO_2 [1] solid solution nanocomposites possessed enhanced oxygen storage capacities. Nanoscaled iron-doped zirconia solid-solution [2] had been discovered with excellent catalytic properties.

In previous studies, rutile TiO_2 materials have emerged as a promising candidate for oxygen detection. However, in most of the researches, rutile TiO_2-based materials must be obtained through high temperature calcination and generally anatase phase transforms into rutile phase at temperatures exceeding 800℃ [3,4]. Crystal particles will suffer grain growth after sintering, which is harmful to the gas sensing properties. Many efforts to prepare rutile TiO_2-based materials at low temperatures had been made, but received tiny effects [5,6].

In latest years, crystal-inducing methods have acquired much attention. Sn^{4+} had been used as crystal-inducing agent in the preparation of rutile TiO_2-based materials for their similarities in both electronic and structural characteristics [7,8]. Series of $Ti_{1-x}Sn_xO_2$ samples had been obtained via the sol-gel process [6], co-precipitation method [5], hydrothermal treatment [9] etc. In most of the researches, the existence of Sn^{4+} may promote the crystallization of rutile nanocrystals and decrease the calcination temperature in a certain degree but cannot avoid the calcination completely. More investigations of $Ti_{1-x}Sn_xO_2$ solid solutions were focused on their functional performances, including the photocatalytic activities [10,11] and gas sensing behaviors [5,12]. It had been reported that TiO_2 doped with appropriate SnO_2 had an improved photocatalytic activity [10,11]. And some studies showed the solid solution exhibited better responses to reducing gases compared with single SnO_2 or TiO_2 [5,12]. However, few attentions had been paid to low temperature synthesis of $Ti_{1-x}Sn_xO_2$ solid solutions and their sensitivity to oxidizing gases.

In this paper, a sol-hydrothermal method was adopted to prepare rutile $Ti_{1-x}Sn_xO_2$ solid solution directly without any high-temperature calcination. The component cations were mixed homogeneously in alkoxides precursors via the sol-gel process, and then uniform sized $Ti_{1-x}Sn_xO_2$

nanoparticles were obtained via the hydrothermal treatment. XRD and TEM were used to characterize the microstructures and morphologies of the products. Oxygen sensing tests of rutile $Ti_{1-x}Sn_xO_2$ powders were also performed to investigate their responses to oxygen.

2. Experimental procedure

2.1. Sample preparation

A certain amount of $SnCl_4 \cdot 5H_2O$ was dissolved in the solution of ethylene glycol and citric acid. Then 1.5mL $Ti(OC_4H_9)_4$ and some water was added under a vigorous stirring to the solution respectively. A mass of white precipitates were appeared. The vigorous stirring was maintained until a transparent sol was obtained. Then the sol was loaded in an autoclave for hydrothermal reaction and kept at 200℃ for 10h. Finally, the products were separated from the solution by centrifugation.

2.2. Physical characterization of the materials

The samples were examined with an X' Pert Pro MPD diffractometer and transmission electron microscopy (JEM-2011). The crystallite sizes and lattice parameters were estimated according to the Scherrer equation: $D\ (hkl) = k\lambda/(\beta \cos\theta)$.

2.3. Gas sensing characterization

In the present study, the test sensors were exposed to O_2 with different concentrations in a static system [13]. The electrical characteristics of the sensor were observed by changing the operating temperature or the concentration of O_2. The concentrations of O_2 were adjusted with N_2 of 99.99% purity. The operating temperatures were controlled by regulating DC powers supplied to the heater.

The gas response, S, is defined as: $S = R_{gas}/ R_{base}$. Here R_{gas} is the resistance of the sensors when exposed to the analyte gas with different concentrations and R_{base} is the resistance of the sample when exposed to ultra high purity N_2.

3. Results and discussion

3.1. Crystalline structure and morphological characterization

As shown in Fig. 1, when Sn^{4+} cotent is above 20%, all products presented the rutile crystalline structure. This suggested rutile TiO_2-based materials (namely $Ti_{1-x}Sn_xO_2$ solid solutions) had been obtained via sol-hydrothermal method with Sn^{4+} as crystal oriented agent. The similarities between rutile TiO_2 and SnO_2 played important roles in this process. Both of them have the rutile crystalline structure [5] and the similar ionic radius of Ti^{4+} (0.068nm) and Sn^{4+} (0.071nm). Thus the mutual substitution of Sn^{4+} and Ti^{4+} in the rutile structure can be realized under certain conditions. And homogeneous mixing of Sn^{4+} and Ti^{4+} on atomic scale via sol route and hydrothermal process may promote the formation of $Ti_{1-x}Sn_xO_2$ solid solutions under relatively mild conditions.

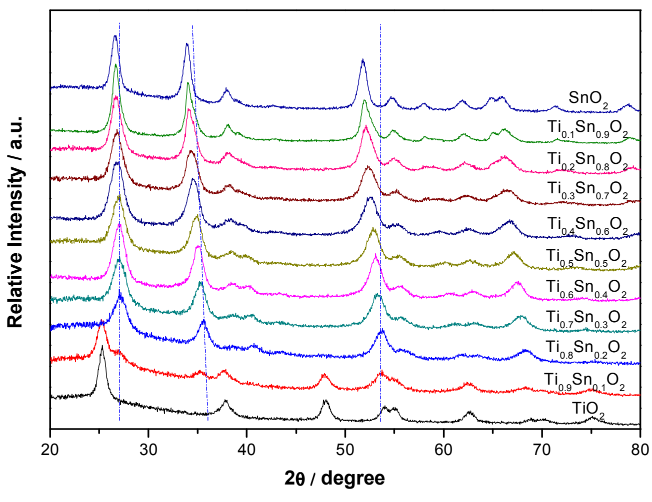

Fig. 1 X-ray diffraction patterns of obtained products

Moreover, diffraction peaks were gradually shifted from rutile TiO_2 to SnO_2 with the increase of Sn^{4+} content. Lattice parameters of the products also verified the gradual changes in diffraction peaks. As shown in Table 1, the lattice parameters increased with the increase of Sn^{4+} mole ratio. This may be ascribed to a slight larger ionic radius of Sn^{4+} (0.071 nm) vs. Ti^{4+} (0.068 nm).

Table 1 Lattice parameters (a, c) of the obtained $Ti_{1-x}Sn_xO_2$ ($0.2 \leq x \leq 1$)

	$Ti_{0.8}Sn_{0.2}O_2$	$Ti_{0.7}Sn_{0.3}O_2$	$Ti_{0.6}Sn_{0.4}O_2$	$Ti_{0.5}Sn_{0.5}O_2$	$Ti_{0.4}Sn_{0.6}O_2$	$Ti_{0.3}Sn_{0.7}O_2$	$Ti_{0.2}Sn_{0.8}O_2$	$Ti_{0.1}Sn_{0.9}O_2$	SnO_2
a	4.6608	4.6668	4.6724	4.6895	4.7009	4.7126	4.7240	4.7242	4.7359
c	2.9981	3.0144	3.0585	3.0644	3.1005	3.1507	3.1655	3.1740	3.1883

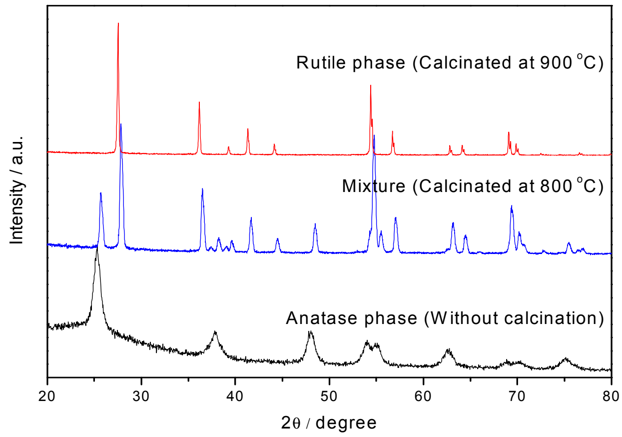

Fig.2 X-ray diffraction patterns of TiO_2 under different calcination temperatures

It was also noticed if there were no sufficient Sn^{4+} crystal-inducing agents, the products were mainly antase samples. In such a case, these antase samples must be annealed at high temperatures to transform to rutile phase. As shown in Fig. 2, the phase transition process completed until after calcination at 900°C. The pronounced narrowing of diffraction peaks implied a remarkable increase in crystallite size which owing to the particles agglomeration during the anneal process. While as shown in Fig. 1, rutile TiO_2-based materials could be obtained directly in the presence of crystal-inducing agent without calcination. The Sn^{4+} incorporation obviously inhibited the crystallization of anatase nanocrystals but promoted the phase transformation from anatase to rutile phase. Therefore it can avoid the particles suffering for exaggerated grain growth due to extra anneal process, which would benefit their oxygen sensing properties.

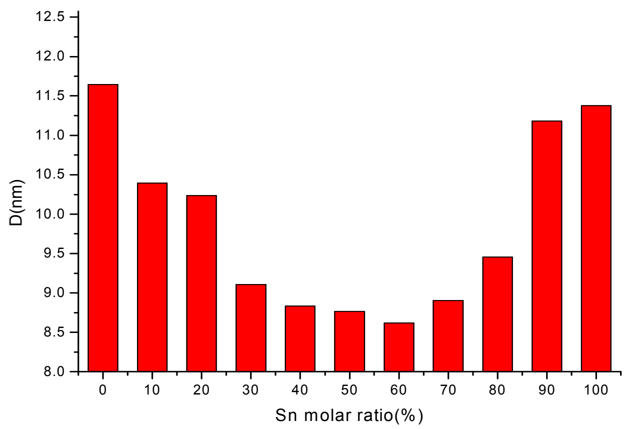

Fig. 3 The crystallite size (D) of obtained samples

And on examining Fig. 1, one can notice remarkable changes in the peaks width which is associated with Sn^{4+} content. This indicated obvious changes in crystallite size. In Fig. 3, crystallite sizes of all samples were reported and there was a lower crystallite size in $Ti_{0.6}Sn_{0.4}O_2$-$Ti_{0.3}Sn_{0.7}O_2$.

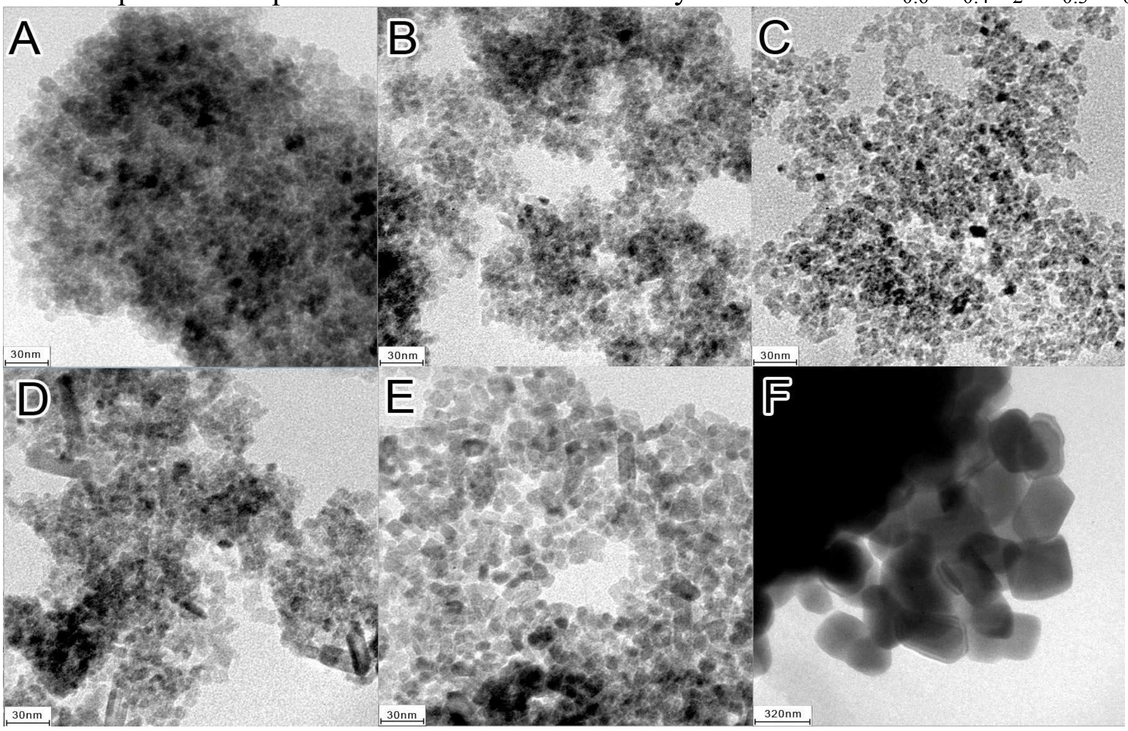

Fig. 4 TEM micrographs of the products: (A) TiO_2; (B) $Ti_{0.7}Sn_{0.3}O_2$; (C) $Ti_{0.5}Sn_{0.5}O_2$; (D) $Ti_{0.3}Sn_{0.7}O_2$; (E) SnO_2; (F) TiO_2 annealed at 900°C

Fig. 4 showed the TEM micrographs of some products. As shown in Fig. 4A-E, those materials were with very fine and well-distributed nanoparticles and the mean crystallite size was about 10nm. The crystallite size of $Ti_{1-x}Sn_xO_2$ is also associated with the Sn^{4+} content. And there is a lower crystallite size in $Ti_{0.6}Sn_{0.4}O_2$-$Ti_{0.3}Sn_{0.7}O_2$. Those are in agreement with the crystallite size analysis in Fig. 3. The sample was subjected to exaggerated grain growth after calcination as shown in Fig. 4F. The specific surface area was decreased, which had bad effects on oxygen sensing properties.

3.2. Gas-sensing properties

It is well known that the gas sensing characteristics of semiconductor materials deeply depend on their catalytic or surface chemical properties, as well as physical or morphological properties, such as grain size, porosity or thickness. In this work, fine and well-distributed rutile $Ti_{1-x}Sn_xO_2$ solid solution nanoparticles had been prepared via a sol-hydrothermal process. Thus the samples have advantage of large specific surface area, which benefits their oxygen sensing properties.

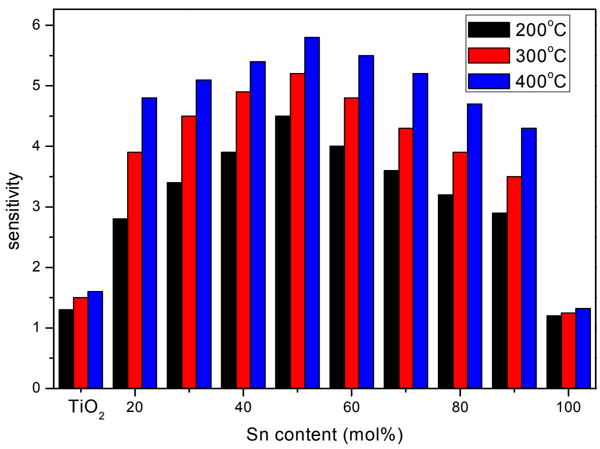

Fig. 5 Sensitivity to O_2 of the obtained samples at different temperatures in 1000ppm O_2

Fig. 5 indicated that the merged oxides exhibited enhanced oxygen sensing properties over either of the individual oxides. Especially, the samples in the composition range of $Ti_{0.7}Sn_{0.3}O_2$-$Ti_{0.3}Sn_{0.7}O_2$ exhibited better oxygen sensing properties than other compositions in all working temperatures which is in accordance with the crystallite size analysis as shown in Fig. 2. Furthermore, the oxygen sensitivities of all compositions were reinforced with the increase of the operating temperature. A typical sample of $Ti_{0.5}Sn_{0.5}O_2$ presented the best sensitivity at 400℃, and the best sensitivity is approximately 6. Results of the gas sensing measurements indicated that rutile $Ti_{1-x}Sn_xO_2$ solid solutions are suitable for oxygen detection at high temperatures.

4. Conclusion

This paper successfully developed a sol-hydrothermal method to prepare rutile $Ti_{1-x}Sn_xO_2$ solid solutions nanoparticles. Hybrid alkoxides of Ti^{4+} and Sn^{4+} were used as precursors in the sol-gel process and Sn^{4+} served as crystal-inducing agent to the formation of rutile crystal lattice in the hydrothermal method. Fine rutile $Ti_{1-x}Sn_xO_2$ ($0.2\leq x <1$) solid solutions nanoparticles with well-distributed crystallite sizes about 10nm had been obtained without any high temperature calcination. The results of oxygen sensing measurements suggested that the rutile $Ti_{1-x}Sn_xO_2$ ($0.2\leq x <1$) solid solution samples exhibited higher oxygen responses than single TiO_2 or SnO_2. A typical sample of $Ti_{0.5}Sn_{0.5}O_2$ presented the best sensitivity is approximately 6 under 400℃.

5. Acknowledgments

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (Proj. No. 60871040 & 60901033).

References

[1] Morikawa A., Kikuta K., Suda A., Shinjo H.. Enhancement of oxygen storage capacity by reductive treatment of Al_2O_3 and CeO_2-ZrO_2 solid solution nanocomposite. Appl. Catal. B-Environ., 2009, 88, pp. 542-549.

[2] Chen L.F., Hu J.C., Richards R.M.. Catalytic properties of nanoscale iron-doped zirconia solid-solution aerogels. ChemPhysChem, 2008, 9, pp. 1069-1078.

[3] Koparde V.N., Cummings P.T.. Phase transformations during sintering of titania nanoparticles. ACS Nano, 2008, 2, pp. 1620-1624.

[4] Carneiro J.T., Savenije T.J., *ET AL*.. How phase composition influences optoelectronic and photocatalytic properties of TiO_2. J. Phys. Chem. C, 2011, 115, pp. 2211-2217.

[5] Carotta M.C., Gherardi S., Guidi V., *ET AL*.. (Ti, Sn)O_2 binary solid solutions for gas sensing: Spectroscopic, optical and transport properties. Sensor Actuat. B, 2008, 130, pp. 38-45.

[6] Ahmed M. A., Yousef E.S., Abdel-Messih M. F.. Preparation and characterization of nanocomposites in system as: SnO_2-xTiO_2 (where x=25, 50 and 75mol%). J. Sol-Gel Sci. Technol., 2011, 60, pp. 58-65.

[7] Shen Q.H., Yang H., Xu Q., Zhu Y., Hao R.. In-situ preparation of TiO_2/SnO_2 nanocrystalline sol for photocatalysis. Mater. Lett., 2010, 64, pp. 442-444.

[8] Yu J.G., Liu S.W., Zhou M.H.. Enhanced photocalytic activity of hollow anatase microspheres by Sn^{4+} incorporation. J. Phys. Chem. C, 2008, 112, pp. 2050-2057.

[9] Hirano M., Dozono H., Kono T.. Hydrothermal synthesis and properties of solid solutions and composite nanoparticles in the TiO_2-SnO_2 system. Mater. Res. Bull., 2011, 46, pp. 1384-1390.

[10] Martínez A.I., Acosta D.R., Cedillo G.. Effect of SnO_2 on the photocatalytical properties of TiO_2 films. Thin Solid Films, 2005, 490, pp. 118-123.

[11] Tu Y.F., Huang S.Y., Sang J.P., Zou X.W.. Synthesis and photocatalytic properties of Sn-doped TiO_2 nanotube arrays. J. Alloys Compd., 2009, 482, pp. 382-387.

[12] Zeng W., Liu T. M., Wang Z. C., Tsukimoto S., Saito M., Ikuhara Y.. Selective detection of formaldehyde gas using a Cd-doped TiO_2-SnO_2 sensor. Sensors, 2009, 9, pp. 9029-9038.

[13] Karunagaran B., Uthirakumar P., Chung S.J., Velumani S., Suh E.-K.. TiO_2 thin film gas sensor for monitoring ammonia. Mater. Charact., 2007, 58, pp. 680-684.

Recent Highlights in Advanced Materials
10.4028/www.scientific.net/KEM.575-576

Synthesis and Oxygen Sensing Properties of $Ti_{1-x}Sn_xO_2$ Solid Solutions Nanoparticles
10.4028/www.scientific.net/KEM.575-576.45