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Preparation of the SnO_2/SiO_2 xerogel with a large specific surface area

Y.S. Feng*, S.M. Zhou, Y. Li, L.D. Zhang

Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, PR China

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Abstract

SnO_2/SiO_2 nanocomposite xerogel was synthesized by using the about-to-gel silica sol as ''nanoglue''. Tin oxide uniformly dispersed within the three-dimension network of the silica in the form of nanoparticles. The SnO_2/SiO_2 nanocomposite xerogel has a large specific surface area (SSA), which depends on the deposition time of the silica sol.

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Keywords: Tin oxide; The SnO_2/SiO_2 xerogel; Specific surface area; Nanogule

1. Introduction

Tin oxide is a kind of wide energy gap semiconductor and has many technological applications in solid-state gas sensors, optical electronic devices, dye-based solar cells and electrodes in thin film [1–4]. Tin oxide nanoparticles shows size-dependent electronic and optical properties, for example, enhancing the sensitivity to many kinds of gas [5–7]. On the other hand, owing to their large surface, they have tendency to aggregate and weak thermal stability, which strongly effect their application. In order to overcome this disadvantage, we prepared the SnO_2/SiO_2 xerogel using the technology analogous to Anderson et al. [8] and Morris et al. [9]. During preparation, the about-to-gel silica solution acted as ''nanogule'' to build three-dimensional silica network. The xerogel networks play an important role in determining the tin oxide nanocrystalline size, confining their growth and retarding their motion. Tin oxide nanoparticles were dispersed uniformly in xerogel. The obtained xerogel differs from the glass-ceramic composite prepared in suit by Chiodini et al. [10]. In glass-ceramic composite, the tin oxide nanoparticles were enwrapped by silica, and gas transport paths were interrupted. The measured gas did not react directly with tin oxide surface; the sensitivity of tin oxide nanoparticles may be suppressed. The xerogel composite in this paper remained large specific surface area; tin oxide nanoparticles in mesoporous silica are in contact with atmosphere and presents good sensitivity to reductive gas.

* Corresponding author. Fax: +86-551-5591434.
E-mail addresses: zyzhao@mail.issp.ac.cn, yisi_feng@mail.issp.ac.cn (Y.S. Feng).

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2. Experimental

The colloidal suspension of tin oxide nanoparticles was prepared by the method described in Ref. [11]. The colloidal suspension has tin oxide content about 10 wt.%. The silica sol was prepared according to the typical method [12] as follows: tetraethoxysilane (TEOS), alcohol and water (molar ratio TEOS/H_2O/C_2H_5OH 1:5:10) were mixed under vigorous stirring; aqueous ammonia (20 wt.%) were dropped into the mixed solution to make pH to 9. After stirring 6 h, the solution became transparent, and then was deposited at room temperature for 36 h.

The two kinds of the solution were combined and stirred 1 min (molar ratio Sn/Si 10%), then the mixture was poured into a petri dish (Φ 120 mm) and covered with parafilm. The petri dish was placed into oven at 60 °C for 12 days and 80 °C for 6 days. Finally, the monolithic samples were obtained with the milkiness color. The monolithic samples were annealed firstly at 300 °C for 1 h and then at 600 °C for an hour. The obtained xerogel composite samples (as the SnO_2/SiO_2 sample) were transparent with colorless.

X-ray diffraction (XRD) measurements were carried out on a Philips diffractometer using a PW 1700 goniometer. The transmission electron microscopy (TEM) and high-resolution TEM were carried out on JEOL-2011 spectrograph. Nitrogen sorption isothermal measurement was conducted on an Omnisorp 100CX porosity analyzer. From the sorption data, the specific surface area (SSA) for the obtained samples was evaluated by using the Brunauer–Emmett–Teller equation. The X-ray photoelectron spectroscopy (XPS) was performed on VG ESCALAB MKII instruments.

3. Results and discussion

Fig. 1 shows the XRD patterns of the SnO_2/SiO_2 sample. The peaks are broad and fit well with the previous reported values of the cassieterite SnO_2 (JCPDS 1983 41-1445). These indicate tin oxide is formed in the sample with small size. On the other hand, the XRD spectrum does not reveal any other phase except the characteristic peaks of tin oxide. This result evidences that the direct chemical interaction of

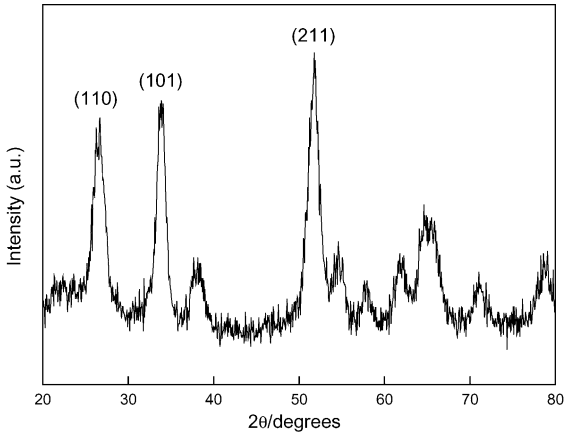

Fig. 1. XRD patterns of the SiO_2/SnO_2 sample.

SnO_2 with SiO_2 does not occur in the composite xerogel.

Fig. 2a shows a bright field TEM micrographs image of the SnO_2/SiO_2 sample with the selected electron area diffraction (SAED) pattern. Tin oxide presents as slightly elliptical particles uniformly dispersed in the silica xerogel network. Tin oxide nanoparticles are about 5–7 nm in diameter. The corresponding SAED result also confirms the nanoparticles are cassieterite SnO_2 phase. Further information about the SnO_2/SiO_2 sample is discussed by high-resolution TEM investigation, as shown in Fig. 2b. Tin oxide nanoparticles are surrounded by amorphous silica. Several domains of the lattice are apparent which have spacing of 0.268 nm, corresponding to the (101) face of tin oxide.

The nitrogen sorption isotherm measurement shows the SnO_2/SiO_2 nanocomposite xerogel presents typical IV adsorption and has a large SSA about 516 m^2/g. Primary experiment indicates that the SSA of the SnO_2/SiO_2 sample is effected by the silica deposition time before mixing with the colloidal suspension of tin oxide nanoparticles. The SSA of the SnO_2/SiO_2 nanocomposite increases from 383 to 516 m^2/g by prolonging the silica sol deposition time from 1 to 36 h. To understand the SSA change with the silica sol deposition time, the Si_{2p} XPS was measured (as shown in Fig. 3). For the sample, the silica sol deposited for 1 h, the XPS spectra (Fig. 3a) presented double peaks with $E_b = 102.8$ and 103.4 eV corresponding to the Si_{2p} of SiO_x ($x < 2$) and

SiO_2, respectively. For the sample, the silica sol deposited 36 h, the XPS spectra (Fig. 3b) presents single peak with $E_b = 103.3$ eV corresponding to the Si_{2p} of SiO_2. Additionally, the gelation time for the mixture solution of the tin oxide colloidal suspension and the silica sol deposited for 36 h is much shorter

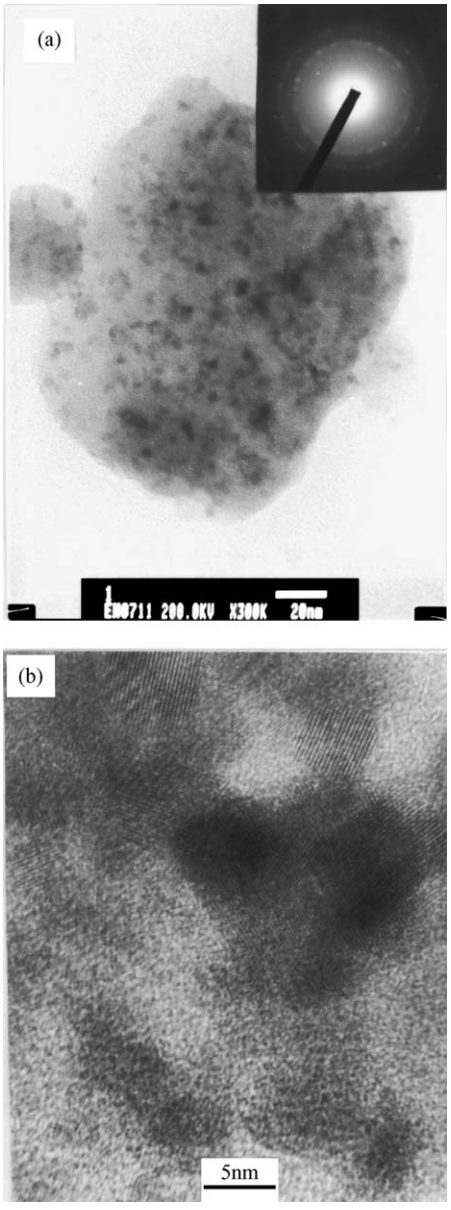

Fig. 2. (a) Transmission electron micrographs with the selected area electron diffraction (SAED) pattern and (b) high-resolution transmission electron micrographs of the SnO_2/SiO_2 sample.

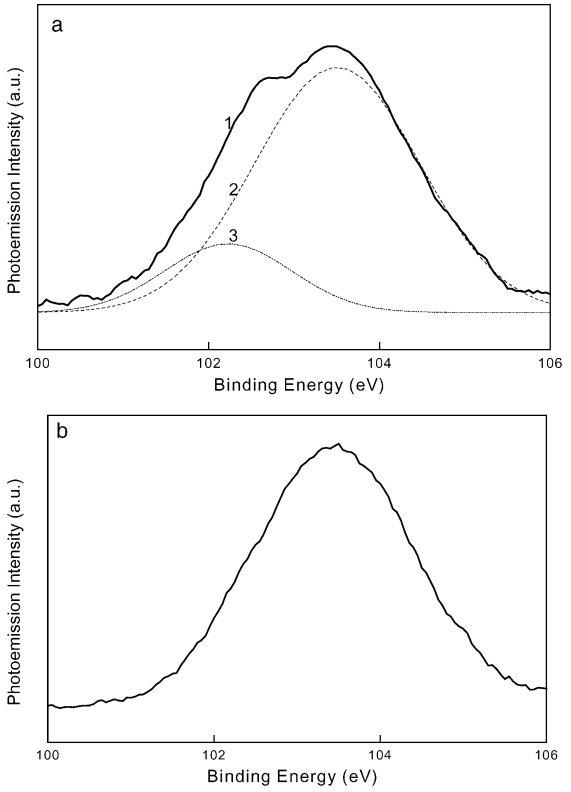

Fig. 3. Si_{2p} XPS spectrum of the SnO_2/SiO_2 sample (a) with silica sol depositing 1 h (curve 1), the spectrum was curve fitted with two Gaussian sum peaks: curve 2 to SiO_x ($x < 2$) and curve 3 to SiO_2, (b) with silica sol deposition 36 h.

(<2 h) than that of the silica sol deposited for 1 h (>12 h). According to the gelation time and the Si_{2p} XPS result, we speculate that the colloidal suspension of tin oxide forbids the silica sol to continue hydrolyze and to condense to form three-dimension networks of silica particles. When silica sol was deposited for 36 h, the silica particle already connected to form networks and the nanocomposite xerogel maintains complete mesoporous constructor.

4. Summary

We prepared the SnO_2/SiO_2 nanocomposite xerogel using the about-to-gel silica sol as nanoglue. Tin oxide disperses uniformly within the three-dimension networks of silica particles in the form of the nanoparticles. The silica network played very

important role in determining the tin oxide size, retarding their motion and confining their growth. The obtained SiO_2/SnO_2 nanocomposite xerogel is in the monolithic form and takes on the large SSA, which is very important for their application especially in the solid-stated gas sensitive field. The formation mechanism and application for SiO_2/SnO_2 nanocomposite xerogel will be the subject of our future intensive study.

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