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Synthesis of mesoporous tin dioxide via sol-gel process assisted by resorcinol–formaldehyde gel

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ABSTRACT

Tin dioxide is a useful *n*-type oxide semiconductor used in a variety of applications owing to its superior optical, electrical, and multifunctional properties. Here, we used a network of resorcinol–formaldehyde (RF) gel to synthesize mesoporous tin dioxide via a sol–gel process. The effects of various synthesis parameters on the morphology and mesoporosity of the obtained product were investigated, including aging time of the RF gel, tin-to-formaldehyde molar ratio, resorcinol-to-carbonate molar ratio, and the aging time of the tin/RF mixed gel. Our experimental results showed that the interaction between the network of the RF gel and tin-containing sol is a key factor that affected the structural strength of the porous network and the porosity of the final product. Through control of the interactions in the tin/RF mixed gel we obtained porous tin dioxide materials that could be effectively used to form large-surface area films with desirable mesoporous properties.

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Introduction

Owing to its remarkable optical, electrical, and mechanical properties, tin dioxide (SnO_2) is considered a particularly useful *n*-type oxide semiconductor, with a broad energy band gap of 3.6–3.8 eV. Although bulk SnO_2 is already used in many applications, mesoporous SnO_2 has potential for use in fields, such as catalysis (Zhang, Huang, & Popov, 2010), gas sensing (Jin, Zhou, Jin, Savinelli, & Liu, 1998; Shimizu, Jono, Hyodo, & Egashira, 2005), photoelectrochemical cells (Toupance, Babot, Jousseau, & Vilaca, 2003), and lithium battery anodes (Wen, Wang, Zhang, & Li, 2007). Various approaches for preparing mesoporous SnO_2 have been reported, including hydrothermal synthesis (Fujihara et al., 2004; Wen et al., 2007), spray pyrolysis (Hieda, Hyodo, Shimizu, & Egashira, 2008), chemical vapor deposition (Bruno, Pijolat & Lalauze, 1994), precipitation (Song & Kim, 2000), and sol–gel processes (Chen & Liu, 1999; Emons, Li & Nazar, 2002; Toupance et al., 2003). Among these techniques, sol–gel processes are particularly attractive because of their simplicity, ambient temperature processing conditions, and formation of products with good homogeneity and narrow size distributions.

To induce mesoporosity within a material, a surfactant is often incorporated as a template (Ahmed et al., 2008; Yu & Frech, 2002; Zhou, Lu, Ke, & Li, 2003). However, common surfactants used in the syntheses of mesoporous SnO_2 result in the uncontrollable formation of microporous structures and a mixture of micro- and mesoporous structures (Li et al., 2008; Xi et al., 2008). Material properties show a strong dependence on the structure, and potential applications of mesoporous SnO_2 require materials with high crystallinity and high surface areas. In general, surfactants decompose at relatively low temperatures and are ineffective for preventing the collapse of pores during calcination. However, calcination at high temperatures is necessary to induce high crystallization in mesoporous tin dioxide. According to the previous studies, calcination at 400 °C is insufficient to completely remove the surfactant from the product (Chen & Liu, 1999; Wang, Ma, Sun, & Li, 2001; Jain, Rashmi, & Lakshmikummar, 2005). As a result, crystallization of SnO_2 is hindered owing to the presence of residual surfactant. Crystallization can be enhanced by increasing the calcination temperature to 600 °C, to completely remove the surfactant (Jain et al., 2005); however, this generally results in an unstable structure and loss of mesoporosity, which reduces the surface area (Guo et al., 2011; Ahmad, Abu Bakar, & Jusliha, 2016). These factors have limited the practical applications of mesoporous SnO_2 (Toupance et al., 2003; Hyodo, Nishida, Shimizu, & Egashira, 2001).

Resorcinol–formaldehyde gel (RF gel) has been recognized as a template for mesoporous carbon aerogels that have surface areas

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as high as 1000 m²/g. The decomposition temperature of this gel is approximately 500 °C, which makes it suitable for synthesis of high-temperature materials (Babic, Kaluderovic, Vracar, & Krstajic, 2004; Jirglova & Maldonado-Hodar, 2010; Luyjew, Tonanon, & Pavarajarn, 2008). RF gel is a product derived from the polycondensation between resorcinol and formaldehyde catalyzed by sodium carbonate (Pekala, 1989). The process is not a direct templating because the interactions between the RF mixture and precursors for sol–gel synthesis of a desired material usually occur (Chantam & Pavarajarn, 2012). For this reason, RF gel is a potentially interesting alternative template for forming stable and well-crystallized mesoporous SnO₂ at high calcination temperatures. Herein, mesoporous SnO₂ was synthesized with an RF gel template. The aim of this work was to investigate the interactions between the tin-precursor and the RF gel by studying the effects of synthesis conditions on the characteristics of the mesoporous tin dioxide. Our approach offers a way to systematically and precisely control the mesoporosity of SnO₂.

Experimental

Preparation of preformed tin-containing sol

The tin-precursor, i.e., tin chloride pentahydrate (Sigma–Aldrich, Milwaukee, WI), reacted vigorously with the RF gel, resulting in rapid solidification of the mixture; hence, a tin-containing sol was first prepared by dissolving the tin-precursor in formaldehyde (CH₂O, Asia Pacific Specialty Chemical, Sydney, Australia). The molar ratio of Sn/CH₂O was varied from 0.003 to 0.06. The solution was stirred for 15 min before aging at room temperature for a predetermined period of time.

Preparation of resorcinol–formaldehyde gel

Resorcinol (C₆H₆O₂, Asia Pacific Specialty Chemical, Sydney, Australia) was dissolved in deionized water (H₂O) and stirred until C₆H₆O₂ was completely dissolved. The C₆H₆O₂/H₂O molar ratio was maintained at 0.15. Next, sodium carbonate (Na₂CO₃, Asia Pacific Specialty Chemical, Sydney, Australia), used as the catalyst for RF gel formation, was added to the solution at C₆H₆O₂/Na₂CO₃ molar ratio in the range of 50–300. CH₂O was then added to the mixture in the last step to give an C₆H₆O₂/CH₂O molar ratio of 0.5. The mixture was stirred until the dissolution was complete before being aged at room temperature for 1–4 h.

Synthesis of porous tin dioxide

Ethanol (C₂H₆O, VWR International S.A.S., France) was added to the aged-RF gel with an C₂H₆O-to-C₆H₆O₂ molar ratio of 5.0 and was stirred for 15 min. The preformed tin-containing sol was added to the RF gel. The Sn/C₆H₆O₂ molar ratio was maintained at 0.08. The mixture was stirred until it became homogeneous and then aged at room temperature for 0–5 days. The aged gel was then immersed in *t*-butanol for 3 days, with replacement of fresh *t*-butanol each day. The washed gel was frozen at –40 °C for 24 h before being freeze-dried for another 24 h. Porous SnO₂ was obtained after calcination at a controlled temperature in the range 400–700 °C for 6 h with a heating rate of 5 °C/min to remove the carbon from the composite.

Product characterization

Nitrogen adsorption/desorption isotherms were measured using a Brunauer–Emmett–Teller analyzer (BET, Belsorp mini II, Tokyo, Japan) to investigate the specific surface area and pore-

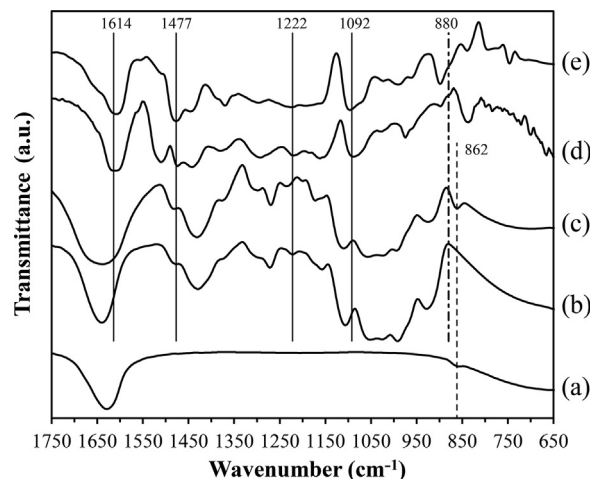


Fig 1. Typical FTIR spectra of SnCl₄ (a), formaldehyde (b), tin-containing sol (c), neat RF gel (d), and Sn/RF composite (e).

size distribution of the samples. The average pore size was obtained by the Barrett–Joyner–Halenda (BJH) method. Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Waltham, MA) was used to identify the chemical functional groups in the gels. The microstructure and morphology of the samples were examined by scanning electron microscopy (SEM, JEOL JSM6400, Tokyo, Japan). The crystalline phases of the products were investigated by X-ray diffraction (XRD, Bruker AXS D8 Advance, Karlsruhe, Germany), while the thermal decomposition behavior was determined by thermogravimetric analysis (TGA, Mettler-Toledo TGA/DSC1 STARE, Greifensee, Switzerland).

Results and discussion

Product characteristics

Without any special treatments, the RF gel mixture reacted violently with the tin-precursor, causing the gel to solidify almost instantaneously. Hence, a tin-containing sol was formed prior to the addition to the RF gel to decrease the activity of the tin-precursor and enable a uniform distribution of the tin within the Sn/RF mixture. To investigate the interaction between the tin-containing sol and the RF gel template, FTIR spectra of the samples at various stages of the synthesis are compared in Fig. 1.

FTIR spectrum of the tin-containing sol showed the presence of formaldehyde. The absorption band of the tin-precursor at 1633 cm⁻¹ merged into a broad band with the signal at 1640 cm⁻¹ arising from formaldehyde. The band from the tin-precursor at 862 cm⁻¹ could also be seen in the tin-containing sol. When the tin-containing sol was mixed with the RF gel, the obtained Sn/RF composite shared the main features of the RF gel, i.e., the C=C stretching vibration of the aromatic rings at 1614 cm⁻¹, the CH₂ stretching vibration of the methylene bridge at 1477 cm⁻¹, and the C–O–C stretching vibrations of the methylene ether bridge at 1222 and 1092 cm⁻¹ (Pekala, 1989; Poljansek & Krajnc, 2005). The signal at 862 cm⁻¹ from the tin-precursor was no longer detectable in the spectrum of the Sn/RF composite. Instead, a signal at 880 cm⁻¹ corresponding to Sn–O–C (Krissanasaerane, Supaphol, & Wongkasemjit, 2010) appeared as a shoulder of the absorption band at 896 cm⁻¹ of the RF gel. This result indicates that an interaction existed between the tin-containing sol and the RF gel. Owing to overlapping of the bands, the intensity of the band at 880 cm⁻¹ was determined by processing the spectrum by Fourier self-deconvolution.

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