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# Effect of water ethanol solvents mixture on textural and gas sensing properties of tin oxide prepared using epoxide-assisted sol–gel process and dried at ambient pressure

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ABSTRACT

High-surface-area tin oxide aerogels have been synthesized by an ambient-pressure drying method, using a non-alkoxide tin precursor and a hybrid sol–gel technique. The tin precursor was dissolved in different volume ratios of mixed water and ethanol solvents, and gelation was attained by means of an epoxide-initiated gelation process. The solvent in the gel was successively replaced with low-surface-tension solvents, and finally the gels were dried at ambient pressure in an oven. It was observed that solvent combinations significantly altered the textural properties of tin oxide aerogels. The solvent exchange process used prior to ambient-pressure drying helped to minimize impurities originating from the tin precursor. The tin oxide aerogels had the maximum specific surface area of 209 $m^2/g$ and small crystallite size (<6.5 nm) after an annealing treatment at 500 °C for 2 h. The sensitivity of a $SnO_2$ sensor to CO gas was found to be strongly affected as the specific surface area of its constituent tin oxide aerogel was increased from 121 $m^2/g$ to 209 $m^2/g$. This study offers evidence of the effects of tin oxide aerogel's specific surface area upon its gas sensing performance.



## 1. Introduction

Detection of toxic gaseous pollutants and combustible gases has become a crucial need for society. Monitoring the emission of process gases from various combustion processes is highly important for safety monitoring and environmental protection [1]. Various methods can be used to accomplish gas sensing, including gas chromatography, mass spectrometry, semiconductor gas sensors and others [2]. Gas sensors based on solid-state semiconductor materials offer considerable benefits relative to other gas detection methods [3]. Semiconductor metal oxide gas sensors are inexpensive to produce, easy to miniaturize, rugged, and reliable, and can be designed to operate over a range of conditions including high temperatures. Tin dioxide ($SnO_2$) is an n-type semiconductor material (room temperature band gap 3.6 eV), largely used as transparent conductive layers [4], as an anode material in Li ion batteries, and as a carrier for supported catalysts [5]. Tin oxide is highly reactive in reducing gases at relatively low operating temperatures, due to easy adsorption of oxygen at its surface because of its availability of natural defects and nonstoichiometric tetragonal $SnO_2$ crystal structure [1,6]. It is well known that the performance of a $SnO_2$ gas sensor is directly related to the $SnO_2$'s particle size, porosity, particle connections, and compositional characteristics (i.e. the presence of additives) [6]. $SnO_2$ gas sensor performance (stability, sensitivity, and selectivity) has been improved considerably by reducing the size of the $SnO_2$ particles to nanometre dimensions [7,8]. Gas sensing by using materials of nanometre crystallite size exposes more reaction sites to the oxidizing or reducing gas due to the enhanced surface area. However, reduction of the particle size of metal oxide below about 3–5 nm will significantly worsen the material's mechanical properties [6]. Therefore, in the present work we synthesized tin oxide aerogels by using a hybrid sol–gel process. The most important advantage of sol–gel process was the ability to tailor the microstructure of the metal oxide material, there by inducing porosity into it. Two different methods are generally used in the sol–gel synthesis of $SnO_2$. The first consists of hydrolysis of a tin alkoxide [9], followed by supercritical drying of

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the resulting gels. This procedure has the advantage of minimizing the impurities in the final material, but is inconvenient owing to the high cost of the precursors and the short-time stability of the sols. For this reason, sol–gel preparation of $SnO_2$ is more commonly achieved by means of hydrolysis of inexpensive precursors such as $SnCl_2$ or $SnCl_4$ [10], by various solution methods [11]. In the present work, a different route was used for the preparation of $SnO_2$ aerogels to minimize impurities in the final material. $SnCl_4$ was used as a tin precursor and gelation was carried out by means of an epoxide-initiated gelation process [4,12]. Attempts were made to synthesize porous tin oxide aerogels with small crystallites by ambient-pressure drying process. Sol–gel parameters of the tin oxide aerogels were optimized and the dependence of the gas sensing performance of tin oxide aerogels upon specific surface area was demonstrated. Generally, aerogels are very light, as they are about 95% porous [1,13]. As prepared tin oxide material by APD process have usually much lower porosity than typical aerogel, therefore here sol–gel synthesized tin oxide material is noted as “high density aerogels”.

## 2. Experimental

All reactants, tin tetrachloride pentahydrate ($SnCl_4 \cdot 5H_2O$), propylene oxide, and ethanol (EtOH), were obtained from Sigma–Aldrich. Tin oxide aerogels were prepared by means of a sol–gel process [13]. Gelation was carried out by means of epoxide-initiated gelation [11] and the gels were dried at ambient pressure drying (APD). Typically, 9.6 mmol of $SnCl_4 \cdot 5H_2O$ was dissolved in 20 ml of a mixed solvent of water and ethanol. This solution was stirred for 15 min. The appearance of solution was little bit opaque. Then, 80 mmol of propylene oxide was added dropwise and stirred for 30 s. Gelation occurred within 2 min, and the gels were placed in an oven at 50 °C for 12 h to strengthen the tin oxide network. After this aging process, the gels were cut into small cubic pieces which were then soaked in a mixed solvent of water and ethanol (50:50 by volume) for 24 h at 50 °C. The gels were then soaked in ethanol for 24 h at 50 °C. The gels were then soaked in hexane for 24 h at 50 °C to exchange the ethanol solvent with hexane. The gel pieces were dried in an oven for 1 h at 50 °C, and then for 2 h at 200 °C. Finally, the resulting dried tin oxide aerogels were annealed for 2 h at 500 °C in air atmosphere. The experimental procedure is illustrated schematically in Fig. 1. This figure also includes photographs of tin oxide aerogel samples prepared by using 25% water solvent and 100% water solvent; these solvents respectively produced sharp and monolithic tin oxide aerogels, and tin oxide aerogel powder. We prepared tin oxide samples by APD process for mixed solvents of water and ethanol with decreasing water content: 100:0 75:25, 50:50, and 25:75, using a fixed amount of solvent. Hereafter these four samples are termed the 100%, 75%, 50%, and 25% water samples. One more sample of tin oxide alcogel, as a reference material was prepared with 25% water mixture solvents with same ratio of chemicals. This alcogel was aged for two days in methanol. Finally, aged alcogel was dried using alcohol supercritical extraction process in an autoclave (Parr Instruments) at a temperature of 265 °C and a pressure of 10 MPa [14]. The structural, textural, and gas sensing properties were analysed of the samples prepared with different compositions of the mixed water and ethanol solvent.

The chemical bonding structure of the tin oxide aerogels was analysed by using Fourier transform infrared (FT-IR) spectroscopy, carried out over the 400–4000 $cm^{-1}$ spectral range by using a Perkin Elmer (model no. 760) IR spectrophotometer. Specific surface area was measured by using a multipoint Brunauer–Emmett–Teller (BET) surface analyser. Pore volume and pore diameter were analysed by using the Barrett–Joyner–Halenda (BJH) method (TriStar 3000 V6.05 A). The porosity and density of tin oxide aerogels were calculated from average pore volume obtained from BJH analysis and standard density of tin oxide (6.95 $g/cm^3$) as a reference value of density. Here the volume of one gram of dense tin oxide is taken as 0.2118 $cm^3/g$ (1/6.95). The total volume of 1 g of tin oxide aerogels is sum of volume of 1 g of tin oxide without porosity and pore volume per 1 g obtained from BJH analysis. Density and porosity were calculated from the following formulae;

$$Density\left(g/cm^3\right) = \frac{1\ g}{Volume\ of\ tin\ oxide\ aerogel\ (cm^3)/g} \quad (1)$$

$$Porosity\ (\%) = \frac{\text{Volume of empty space or pore volume } (cm^3)/g \times 100}{Volume\ of\ tin\ oxide\ aerogel\ (cm^3)/g} \quad (2)$$

The lattice strain was estimated using the Williamson–Hall [15] approach:

$$\frac{\beta \cos\theta}{\lambda} = \frac{1}{D} + 4\varepsilon\frac{\sin\theta}{\lambda} \quad (3)$$

Where D represents the crystallite size and $\varepsilon$ represents the lattice strain. The characteristic Williamson–Hall plot for each XRD spectra were plotted (graph of $\beta\cos\theta/\lambda$ versus $4\sin\theta/\lambda$). Here, $4\sin\theta/\lambda$ is on the x-axis. Each point is assigned to a specific diffraction peaks. After point collection, a linear regression should give a linear fit. The crystalline size was extracted from the y-intercept of a linear fit. The lattice strain ($\varepsilon$) was obtained from the slope of a linear fit line. The surface morphology and elemental composition of tin oxide aerogels was investigated by means of field emission scanning electron microscopy (FESEM; JEOL, JSM 7001F) and energy-dispersive X-ray (EDX) spectroscopy, respectively. The crystalline nature of the tin oxide aerogels was analysed by using a powder X-ray diffractometer (XRD; D/MAX-2000, Rigaku) equipped with a Cu K$\alpha$ radiation source ($\lambda = 1.5418$ Å). For gas sensing, pellets of tin oxide aerogels were prepared at an optimized pressure of 8000 psi and duration of 50 s. For gas sensing, pellets of tin oxide were prepared at an optimized pressure of 8000 psi and a duration of 50 s. Also same weight (0.5 g) was taken to maintain same conditions for all samples. The pellet has circular shape and diameter of sample was 10 mm. The density of each sample pellet was measured by taking ratio of mass and volume of the pellet. The density of tin oxide pellets prepared with 25, 50, 75 and 100% water solvents mixture were 1.96, 2.13, 2.67 and 3.21 $g/cm^3$, respectively. The density of samples was found to be increased after formation of pellets as compared to the density of tin oxide before pellet formation/powder form (Table 1). It was observed that density of pellets were proportional to those of uncompressed powder of tin oxide. Contacts were made between a platinum wire and a pellet of tin oxide by using