



High butane sensitivity and selectivity exhibited by combustion synthesized SnO₂ nanoparticles



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ABSTRACT

We report here the high butane sensitivity and selectivity exhibited by nanoparticles of SnO₂ prepared by a citrate–nitrate gel combustion process. Using the synthesized powders, the sensitivity towards 500, 1000 and 5000 ppm *n*-butane has been measured at various operating temperatures from 350 °C to 500 °C. The powder calcined at 600 °C exhibited a sensitivity of 91 ± 0.5% towards 1000 ppm *n*-butane with a recovery time of 15 s at an operating temperature of 350 °C. We have explored the effect of size on both butane gas sensitivity and selectivity and found that the reduction of particle size of the order of 10 nm could result in a remarkable increase in the response of the sensor towards butane compared to other reducing gases like H₂ and CH₄. The most important observation that emerged from our studies is a combination of sensitivity and selectivity that has been achieved using SnO₂ nanoparticles without the addition of any noble metal catalyst such as Pd or Au.

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1. Introduction

Tin dioxide (SnO₂) is one of the most widely used semiconducting oxides for gas sensor applications due to its high sensitivity, reliability, durability and above all the lower cost [1]. Thick or thin film SnO₂-based gas sensors have been extensively studied to detect a variety of toxic and explosive gases such as CO, hydrocarbons, ammonia, H₂, nitrogen oxides and H₂S [1–26]. The sensitivity of a thick film gas sensor depends mainly on the particle size, shape and their distribution, specific surface area and porosity of the film. Needless to say, all these properties are directly related to the method of preparation of the samples. Thus, preparation techniques that can produce controlled size and shaped particles are of paramount importance in gas sensor development. As a result, many attempts have been made to study the effect of reducing the particle size to nanometric dimension and exploring its consequent effect on the chemical sensing properties [27–32]. When the particle size (*D*) gets reduced to nanometric dimensions, a dramatic improvement in the gas sensing properties could be expected since a large fraction of the atoms are present at the surface or the interface regions with structure and properties different from those of the bulk. The

prominent effect of nano size, however, is associated with the thickness of the electron-depleted surface layer, which is defined as the Debye length '*L_D*'. The Debye length '*L_D*' for a semiconducting material could be calculated as [33],

$$L_D = \frac{\sqrt{\epsilon_0 \epsilon k_B T}}{e^2 n_d} \quad (1)$$

where *k_B* is Boltzmann's constant, ϵ the dielectric constant, ϵ_0 the permittivity of free space, *T* the operating temperature, *e* the electron charge and *n_d* the carrier concentration. For example, *L_D* for SnO₂ has been estimated to be 3 nm. If the particle size is reduced to a size that is comparable to or lower than 2 *L_D*, the whole crystallite is depleted of electrons and this in turn causes the gas sensitivity of the element to change dramatically with *D*. Since *L_D* for SnO₂ is 3 nm, the critical size at which SnO₂ could exhibit the "size related nano- effect" and its consequent impact on gas sensitivity should be around 6 nm or lower. Therefore, in order to improve the gas sensitivity of SnO₂ based materials it is desired to work with nanoparticles having size range within 6 nm. Although there are many reports on the synthesis of nanoparticles of SnO₂ by sonochemical technique, sol–gel processing, co-precipitation technique, hydrothermal route, and gel-combustion route, the studies dealing with the butane gas sensitivity of such materials are rather scarce as evident from the cited references [2–31]. More importantly, to our knowledge most of the reported results are on the sensitivity leaving behind the importance of selectivity untouched and unexplored in most cases [27–33].

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In this paper, we report the synthesis of SnO₂ nanoparticles by a citrate–nitrate process (CNP) and their detailed gas sensing characteristics towards *n*-butane, an important component of the liquefied petroleum gas (LPG). This process could produce homogeneous high surface area powder with superior properties as demonstrated previously by other investigators [34–42]. Though there has been a very few attempts to prepare SnO₂ particles by combustion process [43–47], none has reported the potential of this economically viable process in preparing highly sensitive SnO₂ particles for butane detection. Our interest mainly lies in exploring the sensitivity and selectivity of nanoparticles of SnO₂ prepared by this economically viable process and to understand the effect of particle size on the performance of the sensor made thereof. Interestingly, in the present case, the CNP prepared SnO₂ nanoparticles exhibited a high sensitivity and selectivity with a fast recovery time towards *n*-butane compared to SnO₂ based systems prepared by us by other techniques [48,49].

2. Experimental

2.1. Chemicals

Tin chloride dihydrate, SnCl₂·2H₂O ([MERCK India, GR], citric acid monohydrate, ammonium nitrate, distilled water and absolute ethanol were used. All reagents used were analytically pure.

2.2. Preparation of SnO₂ nanoparticles

To prepare nano particles of tin dioxide, a mixture of an aqueous solution of SnCl₂·2H₂O (0.2 M) and ammonium nitrate solutions were taken in a beaker and calculated amount of citric acid monohydrate was added to this mixed solution keeping the citrate–nitrate molar ratio as 0.3. The rest of the procedure is similar to what has been reported earlier [39–42]. The precursor ash powder obtained was calcined at 600 °C for 6 h in air to remove unburnt carbonaceous material and to form a pure oxide phase. From the concept of propellant chemistry, the net oxidizing valency of metal nitrates to the net reducing valency of fuel should be unity to get the maximum exothermicity for driving the combustion reaction. In our experiments, we have optimized the citrate to nitrate ratio as 0.3 for achieving a satisfactory combustion reaction.

2.3. Characterization

Thermogravimetric analysis (TGA) of the as-prepared gel and uncalcined powder was carried out on a Netzsch (Germany) simultaneous DTA-TGA analyser (Model No. STA 449C) from room temperature to 1000 °C at a heating rate of 10 °C/min. The phase identification of the calcined powder was carried out by X-ray diffraction analysis (Philips PW1710) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The surface area analysis of the calcined powder was measured by the Brunauer–Emmet–Teller (BET) method on Micromeritics Gemini II 2370 equipment. The particle morphology and local crystallographic structure were studied by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM), respectively. The samples for microscopy were prepared by depositing micro-drops of the acetone-dispersed sample on a carbon coated copper grid followed by drying. The average particle size of the calcined powders was calculated using the bright field (BF) image obtained from TEM.

2.4. Gas sensing measurement

For gas sensing study, a thick paste of the powder was prepared using an alumina gel as a binder. The details of the sensor fabrication and processing have been reported elsewhere [48,49].

The consistency of the paste and the processing variables were optimized to get final coatings of 50–60 μm thickness. Using the paste a thin coating was made on the outer surface of the alumina tubes of 3 mm length, 2 mm outer diameter and of 0.5 mm thickness attached with gold electrodes and platinum lead wires. After coating, the sensors were cured at 600 °C for 2 h, so that the sensor surfaces have particles of size comparable to that of the characterized nanoparticles. The electrical resistance of the sensors in air and in *n*-butane was measured at different temperatures (up to 500 °C) in an ambient of 60–70% relative humidity using a digital multimeter (Solartron) and a constant voltage/current source (Keithley 228A). All the samples were initially aged at 350 °C for 72 h to achieve the desired stability of the resistance value before the measurements. The percentage response or sensitivity (%S) of the films was calculated as:

$$(\%)S = \frac{\Delta R}{R_A} = \left[\frac{(R_A - R_G)}{R_A} \right] \times 100 \quad (2)$$

R_A and R_G are the sensor resistances in air and measuring gas, respectively. ΔR for reducing gases is $(R_A - R_G)$ where $R_A > R_G$. The response time has been measured as the time taken for a sensor to read 90% of full-scale reading after being exposed to a given gas and recovery time was the time taken for a sensor to come back to its original state when the target gas is removed.

3. Results and discussion

3.1. Thermal characterization

In order to understand the thermal decomposition behavior of the samples, simultaneous TGA-DTA measurements have been carried out on the gel and the as-prepared SnO₂ powder (Fig. 1(a) & (b)). The gel sample exhibited a weight loss of ~88% whereas the as-prepared powder exhibited a weight loss of only ~25%. The initial weight loss of 3.26% exhibited by the gel sample between 30 °C and 110 °C is well supported by an endothermic peak on the DTA at ~119 °C. These changes are probably due to the dehydration of surface adsorbed water. From 110 °C to 179 °C, a weight loss of 11.24% along with a corresponding exothermic shoulder at 174 °C was observed. From 179 °C to 244 °C, a total weight loss of 14.84% was evident. The above changes were accompanied by an

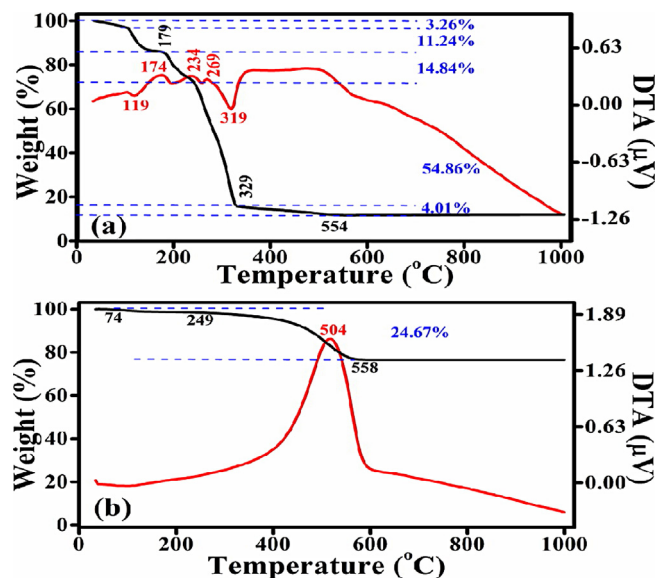


Fig. 1. TG-DTA curves of the (a) gel, (b) as-synthesized SnO₂ powder obtained from citrate–nitrate process.

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