Notes

On the structural, morphological and gas sensing properties of nanocrystalline SnO$_2$

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Received 8 July 2015; revised and accepted 28 August 2015

Tin salt precursor capped by oleic acid under solvothermal conditions gives tetragonal rutile phase of SnO$_2$ with average particle size of 14 nm with a band gap of 4.27 eV. The SnO$_2$ nanoparticles exhibit photoluminescence with an intense purple emission band at 425 nm. The transmission electron micrographs show the growth of nanoparticles in specific orientation. The petroleum gas sensing response of this material decreases with increase of sensing temperature.

**Keywords:** Nanoparticles, Semiconducting oxides, Quantum dots, Gas sensors, Oxides, Tin oxides, Solvothermal method

Semiconducting oxides have been exploited for designed functional devices. Semiconducting oxides have diverse cation valences and tunable oxygen deficiency, which play a role in creating and fine tuning several material properties$^1$. The need of the hour is the ability to control the size and morphological aspects with reproducibility and also to tailor the properties of the material. It has been established that a multitude of properties like optical, magnetic, specific heat, melting point and surface reactivity depend on the size of nanoparticles$^2$. Among the various semiconducting materials, SnO$_2$ is a typical optically transparent n-type semiconductor with a wide band gap of 3.6 eV at 300 K, which can be used for a wide range of applications such as resistors, gas sensors, special coating for energy-conserving 'low-emissivity' windows, transparent heating elements, electrodes in glass melting furnaces and antistatic coating$^3$. It is well known that the size and morphology of the materials greatly affect their properties as well as their applications. Particularly, for SnO$_2$ materials, studies by various research groups have confirmed that their gas sensing performance is affected by several parameters such as particle size, surface-to-volume ratio and crystallinity. For example, small particle size, a large surface-to-volume ratio, and high crystallinity are required to enhance the sensitivity of gas sensors$^4$. The processing of metal oxides and metal sulphides under hydrothermal conditions constitute an important aspect because of advantages in the preparation of highly monodispersed nanoparticles with a good control over size and morphology.

Literature survey indicates several published articles on gas sensing using SnO$_2$. However, SnO$_2$ based quantum dots sensors for liquefied petroleum gas has not been investigated in detail, specifically at low operating temperatures without any noble metal and non-noble metal or metal oxide dopants. Quantum dot particle aggregates exhibit an irregular spherical structure with spherical as well as some rod-like patterns. Nanorods (1D nanostructures) offer large adsorption area for the gaseous species. In particular, material architectures (such as nanorods) are excellent candidates for gas sensing devices because in addition to high surface area, these structures have better and directional charge transfer properties because of the availability of both inner and outer surfaces for gas adsorption$^5$.

The present study deals with the preparation of SnO$_2$ nanoparticles via a low temperature solvothermal method involving water and ethanol as a solvent, which play an important role in the structure and morphology of the nanoparticles formed. Further, SnCl$_2$.2H$_2$O as a precursor is found to be an ideal material for preparing SnO$_2$ nanoparticles with the added advantages of its low cost and environmental friendly nature that facilitates easy removal of the anion. The SnO$_2$ nanoparticles prepared by the solvothermal route were subjected to structural, morphological and optical characterization. The nanopowder was pelletized and its function as a gas sensor was investigated with liquefied petroleum gas (LPG) of varying concentrations and temperature. In gas sensors, response and recovery time are important parameters. Our results show that with the present material, the response time is low.

**Experimental**

SnCl$_2$. 2H$_2$O, ethanol, Oleic acid and NH$_4$OH were of AR (Merck) and used without further purification.
In a typical synthesis of the SnO$_2$ nanoparticles, 0.3 M SnCl$_2$·2H$_2$O was dissolved in 100 mL of deionized water and 50 mL ethanol and stirred at room temperature (37 °C) for 6 h, and then 20 mL of oleic acid was added dropwise to this solution under stirring for 6 h. After stirring, NH$_4$OH was added to the solution with continued stirring with the pH maintained at 12. Then, the resulting solution was transferred and sealed into a 50 mL Teflon-lined stainless steel autoclave and kept in an electrical oven at 85 °C for 10 h. After cooling down to room temperature, the white precipitate obtained was washed with distilled water and ethanol several times, and then dried under vacuum at 60 °C for 5 h.

To identify the crystalline phase and structure, powder X-ray diffraction patterns were recorded on a Bruker Binary V3 powder X-ray diffractometer. The morphology was observed using a Jeol JSM-6700F scanning electron microscope and particle size was measured using a Philips CM 200 TEM microscope at operating voltages: 20-200kV and resolution: 2.4 Å. The UV-visible spectrum was recorded using the double beam Cary 5E spectrophotometer. Photoluminescence of the sample was recorded on a Perkin Elmer Luminescence Spectrometer (LS-55). The SEM images were recorded using a Jeol JSM 6310 scanning electron microscope. The identification of particle morphology and the particles size measurements were conducted using TEM (Jeol JEM 3010). Gas sensing properties were investigated using a conductivity cell fabricated with a sensing chamber and the measurements were made by a two probe technique.

For the gas sensing experiments, the as-prepared SnO$_2$ nanopowder was ground thoroughly along with a binder (PVA) in a mortar and pestle. Then the mixture was subjected to cold pressing in a hydraulic press with a dye of 1 cm diameter by applying a pressure of 5 tons/mm$^2$. The freshly prepared pellet was then sintered at 300 °C for an hour to provide physical strength and solid state electrical properties due to the reactions within the pellet components and partly due to O$_2$ in air. After the sintering process was over, the pellet was removed from the furnace and allowed to cool naturally for about one hour before using it as a sensor in a dedicator. The sensing element was made with the help of silver paste to make Ohmic contact. The gas sensing study to sense the LPG in air was carried out in a static gas chamber. The sensor was placed directly on a heater in the gas chamber and then tested for sensing properties for variable temperatures. Chromel-alumel thermocouple was kept in contact with the sensor to monitor the temperature. Before the introduction of the LPG, the gas chamber was prefilled with air and maintained at atmospheric pressure. The sensor was allowed to establish equilibrium inside the gas chamber for about 1 h at the operating temperature. The experiments were repeated several times to measure the sensitivity as a function of the operating temperature.

Keithley electrometer (model 2400) was used to determine the electrical resistance of the sensor, both before and after exposing it to LPG. The exposure time of the gas was maintained as 10 min for all the measurements. The response time was found to vary between 50 and 60 s and the corresponding recovery time was around 4–5 min. To investigate the gas sensing properties of SnO$_2$ nanoparticles, the fabricated sensor was tested at different temperatures ranging from 200–350 °C in steps of 50 °C to optimize the working temperature. The sensitivity was measured with LPG at concentrations of 500, 1000, 1500 and 2000 ppm.

### Results and discussion

All of the diffraction peaks in the pattern (Fig. 1) are in good agreement with tetragonal SnO$_2$ (JCPDS No. 41-1445) $a = 0.4738$ nm and $c = 0.3187$ nm, which confirms that SnO$_2$ was be obtained by solvothermal technique. Some other sharp peaks indicate the crystalline nature of the sample. No other crystallographic phase could be detected. The broad reflection profiles are due to the very small crystallite size of the nanostructured materials. By using Scherer’s formula, the mean crystallite size of the SnO$_2$ nanoparticles was calculated to be about 14 nm.
UV-vis absorption spectrum recorded for the SnO$_2$ nanoparticles is shown in Fig. 2. The SnO$_2$ nanoparticles synthesized by solvothermal process show a band gap of 4.27 eV. The band gap value obtained from Tauc’s plot (Fig. 2 (inset) of the sample is shifted to higher energies (i.e., a blue shift) when compared to the bulk SnO$_2$, thus confirming the quantum confinement effect in the obtained nanoparticles. This band gap shift suggests that the size and shape of the nanoparticles determine the electronic properties of the materials.

In the past few years, several studies on the room temperature photoluminescence (PL) of SnO$_2$ nanostructures have been reported. Room temperature red light emission with a peak at ~605 nm (2.05 eV) due to oxygen vacancies was observed in SnO$_2$ nanorods and beaklike SnO$_2$ nanorods. Recently, room temperature blue light emission with a peak position at ~445 nm (2.8 eV) due to a triplet-to-ground-state transition at a neutral oxygen vacancy defect has been reported in SnO$_2$ nanoblades synthesized by a low temperature hydrothermal process. Figure 3 represents the PL spectrum of SnO$_2$ nanoparticles synthesized via hydrothermal process. The room temperature PL spectrum of the sample shows a single sharp peak at around 425 nm. The peak represents the blue emission of the SnO$_2$ quantum dots and the observed peak maximum matches with that of the earlier report.

The morphology of the product was observed by the SEM images at high magnification. Figure 4 shows the morphology of the as-prepared SnO$_2$ nanoparticles grown under basic conditions. It is evident that the spherical particles are aggregated with the presence of microspheres. The aggregates exhibit an irregular spherical structure as well as rod-like patterns. The larger spherical aggregates have diameter ~0.7 µm and the smaller rods are in the thickness range of ~80–100 nm. The dark spots indicate a moderate level of agglomeration in the sample.

TEM studies were performed to obtain the particle size distribution and the morphology of the SnO$_2$ nanopowder. The sample was ultrasonically dispersed in ethanol and placed over a carbon grid. It is evident from the low resolution TEM images that there are several tiny particles in the size of 3–4 nm, which are
seen with distinctly spherical morphology. It has been reported that the morphology and crystallinity of tin oxide nanoparticles can be changed with the variation of pH as well as solubility and temperature\(^1\). The high pH of 12.2 along with the solubility line of Sn(II) with water/ethanol solvent is believed to have caused the growth of tiny particles of SnO\(_2\). The TEM micrograph also indicates a moderate level of aggregation caused by the van der Waal forces. At the same time, at a few spots these primary particles are found to coalesce to form rod-like pattern, which possibly indicate the anisotropic growth leading to 1D nanostructure only at selected areas. These SnO\(_2\) nanorods have their aspect ratio ranging from 3–4 nm. Similar observation was made by Birkel’s group\(^1\) for SnO\(_2\) nanoparticles prepared by solvothermal approach with SnCl\(_4\)-5H\(_2\)O and various alkali hydroxides in water/ethanol solvent. The HRTEM micrographs reveal the single crystalline nature of the SnO\(_2\) nanoparticles. The nanostructure is composed of a continuous string of precisely ordered nanoparticles whose lattice fringes are crystalline.

The presence of SnO\(_2\) nanoparticles of size ~ 4 nm is evident from the HRTEM micrograph (Fig. 5(b)). The solvothermally synthesized nanoparticles are expected to provide good sensitivity owing to their smaller grain size. The observed size of the tin dioxide is below the critical grain size, \(D < 2L\) and a space charge depth of \(L = 3\) nm for SnO\(_2\) is likely to provide good sensitivity of the gas\(^8,13\). Further, these nanoparticles are seen to coalesce with each other. These coalesced particles usually give rise to anisotropic growth via oriented attachment mechanism. The oriented attachment mechanism describes the spontaneous self-organization of adjacent particles such that they share a common crystallographic orientation, followed by joining of these particles at a planar interface. The process is particularly relevant in the nanocrystalline regime, where bonding between the particles reduces the overall energy by reducing the surface energy associated with unsatisfied bonds. In the case of solvothermally coarsened metal oxide like TiO\(_2\), the nanoparticles assemble into single crystalline structures composed of several primary crystallites\(^14,15\). The HRTEM images (Fig. 5(c, d)) reveal the oriented attachment of nanoparticles which results in a single crystalline nanorod. The crystallinity of the SnO\(_2\) nanopowder leads to well pronounced Scherrer diffraction rings in the selected area electron diffraction (SAED) pattern (Fig. 5 (e)) and can be assigned to the reflections (110), (101), (200), (211) and (301) of tetragonal SnO\(_2\). The SAED pattern does not show any additional peak and thus confirming that the sample is devoid of impurities.
The response of the metal oxide semiconductor sensors is mainly determined by the interaction between a target gas and the surface of the sensors. Due to the greater surface area of nanostructured materials, its interaction with the adsorbed gases is significant, leading to higher response.16 The design of the new chemical sensing devices using nanomaterials has received considerable interest in the past decade. Conductivity of tin oxide is sensitive to the surrounding atmosphere and hence, can be used in the construction of chemical sensors for explosive or toxic gases and water steam detectors.17 At elevated temperatures, oxygen adsorbs on the surface of the SnO₂ grains, accompanied by electron abstraction from the conduction band. This process creates an electron depleted surface region (or space charge layer), which represents a barrier to electrical conduction between the SnO₂ grains. A combustible gas can react with the surface oxygen species, allowing electrons to be reintroduced to the surface region leading to a decrease in the depth of the space charge layer. Hence, the barrier to inter-grain electrical conduction is reduced and the net observed effect is a drop in the bulk resistance of the nanosized sensing element. For most conventional SnO₂ sensing materials, the grain size is considerably greater than the depth of the space charge region and electrical conduction within the bulk is governed by the grain boundaries. However, nanocrystalline materials offer grain sizes where the depletion layer has dimensions similar to the particles radius, and under these conditions, the electrical conduction is predominantly grain controlled. Thus, when the SnO₂ grains are fully depleted of electrons, very low reducing gas concentrations can have a profound effect on inter-grain conduction. It is expected that under these conditions the gas sensitivity should be directly influenced by the particle size, so that increasing sensitivity should accompany a decrease in particle size. The benefits of incorporating nanostructured materials in sensor films with the aim of achieving high reducing gas sensitivity has attracted growing interest, culminating in the appearance of several recent research reports in the literature.18

Wagh et al.19 have reported the sensing mechanism for LPG detection, using surface ruthenated SnO₂ in which a few of the Sn-O linkages are believed to be replaced by grafting Ru-O linkages resulting in the change in adsorption-desorption kinetics. It is known that the operating principle of thick film tin oxide sensor is based on reactions of gas molecules with O₂ and O⁻ ions previously adsorbed on the sensor surface at an appropriate elevated temperature. The responses of these sensors are based on oxidation-reduction of gas species on the sensor surface, which modulates the conductivity of the sensor.20

Figure 6(a) shows the sensitivity as a function of operating temperature for SnO₂ nanoparticles with LPG. The gas response increases with increase in the operating temperature largely supported by the increase in the surface-to-volume ratio and reaches a maximum at around 250 °C, followed by a decrease in the sensitivity with further increase in the operating temperature. The gas response is seen in the form of a volcano shaped distribution against the operating temperature and indicates that the optimum performance is achieved at 250 °C for LPG. The gas response peak observed for SnO₂ nanoparticles in this work is similar to that reported earlier for Fe₂O₃ doped SnO₂ thin films for LPG but at a relatively higher temperature of 350 °C. However, in the present case no catalyst has been incorporated to improve the response of the material. Notably, the optimum temperature was the same for all the concentrations of LPG considered for this study. The adsorption of O₂ from the air ambient atmosphere makes the sensor to ‘feel’ the LPG presence at lower than the optimum temperature. At the optimum temperature, all the oxygen molecules are replaced by the LPG particles giving a volcano shaped response, again at temperatures above the optimum temperature, the reverse reaction take place. The improved sensitivity can be attributed to the relatively smaller size of the SnO₂ nanoparticles synthesized in the solvothermal condition.

Figure 6(b) shows the sensitivity of the SnO₂ nanoparticles on the LPG concentration at different operating temperatures. The gas response increases nearly linear as the concentration of LPG increases from 500 ppm to 2000 ppm and is maximum at 250 °C. These results also confirm that 250 °C is the optimum temperature for LPG sensing. The variation of sensitivity and exposure time is depicted in Fig.6(c) at different operating temperatures. The variation of resistance of the SnO₂ pellet with time at 1000 ppm and also at 250 °C was studied. The plot of resistance with exposure time for SnO₂ pellets indicates that the resistance decreases rapidly in the initial stage and then remains constant with further increase in temperature and response time.
Herein, crystalline SnO$_2$ nanoparticles were successfully synthesized by an oleic acid assisted solvothermal process. Powder XRD pattern indicates particle size of the nanocrystalline SnO$_2$ to be 14 nm, according to Scherrer formula. Blue shift of the absorption edge may originate from confinement of electrons and holes (quantum size effect) in the defect levels of the band gap. The SnO$_2$ nanoparticles display room temperature PL with an intense purple emission band at 425 nm. SEM images show spherical particles aggregated with microspheres. TEM images confirm formation of nanoparticles of varying sizes (3–6 nm). As gas sensor for detecting LPG, the as-obtained SnO$_2$ nanoparticles exhibit low detecting limit (500–2000 ppm), remarkable sensitivity, good reproducibility and short response/recovery times due to its unique quantum dots nanostructure.

References