A Highly Selective and Fast-Responding Hydrogen Sensor based on In$_2$O$_3$ Nanocubes

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Abstract: The In$_2$O$_3$ nanocubes were successfully synthesized without any templates by calcining the In(OH)$_3$ precursor in air at 300°C for 2 h and their H$_2$ sensing characteristics were investigated. The In(OH)$_3$ precursor was prepared through a wet chemical route at room temperature (27°C) using InCl$_3$, 4H$_2$O and NH$_3$OH$_3$ starting materials. The formation of In$_2$O$_3$ nanocubes was confirmed by X-ray diffraction measurement (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) analysis. The In$_2$O$_3$ nanocubes exhibit excellent $H_2$ sensing properties such as, high gas response (~130 to 50 ppm H$_2$ at 325°C), extremely rapid response (1s), fast recovery (~5 s), excellent repeatability and good selectivity. Furthermore, the lower detection limit is ~3.87 ppm, which is lower than the permissible explosive limit for H$_2$. The experimental results demonstrate the potential of the In$_2$O$_3$ nanocubes as sensing material in the fabrication of hydrogen sensors.

Keywords: In$_2$O$_3$, nanocubes, H$_2$ sensor, Semiconductor gas sensors, TEM, XRD.

1. Introduction

Hydrogen (H$_2$) gas, due to its efficient fuel properties like high burning velocity, large heat of combustion (142 kJ/g), low minimum ignition energy (0.017 mJ) and wide flammable range (4–75%), offers its candidacy for future generation energy source[1]. The burning product of hydrogen is water which is clean and can again be converted into hydrogen and oxygen. This property further makes it a clean and renewable energy fuel source for cars, buses, and other vehicles [2]. Liquid hydrogen is used as a fuel for rockets. Monitoring/controlling of the hydrogen concentration is also crucial in nuclear reactors, coal mines and semiconductor manufacturing. [3–5]. However, hydrogen gas is tasteless, colourless, odourless and leaks with large diffusion coefficient (0.61 cm$^2$/s). It catches fire even at low volume concentrations (>4 ppm) and has large flame propagation velocity [6–8]. Therefore, uses of hydrogen in technological applications are generally associated with effective execution of sensors to detect or critically monitor minute hydrogen leakages.

Semiconductor metal oxides are historically and generally investigated as hydrogen sensors. V. Aroutioumian [9] has reviewed, compiled and tabulated some important data (from 1966 to 2006) about hydrogen sensing properties metal oxides along with effect of doping by metal nano particles and another metal oxide. Recently, Haoshuang et. al [1] have provided a comprehensive review on the hydrogen gas sensors based on metal oxide thin films and one-dimensional (1D) nanostructures for the period 2007-2012 in which the hydrogen sensing mechanism and some critical issues are discussed. The influences of grain size, porosity, orientation, doping and surface decoration as well as the device architecture on the sensing performance of hydrogen sensors is also widely investigated for improving gas selectivity and hydrogen response at low temperatures.

Recently, Wadkar et.al [10] have reported a high performance H$_2$ sensor based on ZnSnO$_3$ cubic crystallites synthesized by a hydrothermal method. Amongst other recent studies, Katoch et. al [11] have reported SnO$_2$–ZnO nano fiber composite for drastically enhancing the sensing behavior H$_2$ gas and Wang et.al [12] report a low temperature, high performance hydrogen gas sensors using palladium decorated tungsten oxide.

Indium oxide (In$_2$O$_3$) is an important wide band gap (3.55–3.75 eV), transparent material with attractive optoelectronic properties suitable for applications in solar cells[13]. It has received considerable attention because of its high electron affinity and low electron effective mass and increasingly extensive applications in fuel cells [14–15], sensors [16], nano scale transistors [17] and flat-panel display materials [18]. In$_2$O$_3$, as a n-type semiconductor, has proven to be a highly sensitive material for the detection of both reducing and oxidizing gases [19]. Few research groups have recently studied H$_2$ sensors based on pure In$_2$O$_3$ nanostructures with different morphologies [21, 22]. Qurashi et. al [20] reported the H$_2$ sensor based on In$_2$O$_3$ nano wires (~70 nm) and nano needles (150–200 nm) synthesized via catalyt supported growth by vapor transport. The In$_2$O$_3$ nanowires showed a maximum response of about 0.6 at 400°C with the response and recovery times of ~31 s and ~80 s for 500 ppm of H$_2$ at 200°C, respectively. The nano needles exhibited a maximum response of 0.25 at 350°C with response time of 60 s. More recently, Zheng et. al [21] reported hydrogen sensing properties of In$_2$O$_3$ nano towers with an octahedral cap size of 600 nm synthesized via thermal evaporation of In$_2$O$_3$ and active carbon powders. The In$_2$O$_3$ nano towers showed a high response of 83 % towards 1000 ppm of H$_2$ at 240°C with a response time of 63 s. The detailed study on the influence of morphology of In$_2$O$_3$ on the H$_2$ gas sensing properties was reported recently by Shannugasundaram et. al. [22]. These authors prepared the In$_2$O$_3$, having different morphologies like nanobricks(200 nm × 200 nm × 50 nm) nano particles (10–20 nm), mesoporous nanocubes (200 nm × 200 nm × 200 nm) and nanoflakes by using a facile hydrothermal route. This study unambiguously demonstrated that the sensing performance of nanocubes is far more superior than the other
morphologies. The In$_2$O$_3$ nanocubes sensor exhibited response of 980 with the response and recovery times of ~39 s and ~115 s for 0.5 ppm of H$_2$ at 150 °C, respectively.

Within the present investigation, experiments have been carried out for the fabrication of a highly selective and fast responding H$_2$ sensor based on In$_2$O$_3$ cubic crystallites. In this study, the In$_2$O$_3$ cubic crystallites were synthesized through a wet chemical route at room temperature. Sensing characteristics of the In$_2$O$_3$ cubic crystallites to H$_2$ were systematically investigated. A sensing mechanism is also discussed based on experimental findings.

2. Experimental

2.1 Materials

All of the chemicals were of analytical grade and were used as-received without any further purification. The indium chloride tetrahydride (InCl$_3$, 4H$_2$O) and liquid ammonia (NH$_3$) solution(30%) were purchased from John Baker Inc-Colorado, U.S.A. and Qualigens Fine Chemicals, India, respectively.

2.2 Synthesis of the In$_2$O$_3$ nanocubes

In a typical synthesis of In$_2$O$_3$ nanocubes, 0.29 g of InCl$_3$, 4H$_2$O was dissolved to double distilled water (10 mL) to form a solution A. The liquid NH$_3$ (5 mL) was added to double distilled water (5 mL) to form a solution B. The solutions A and B were slowly added drop-wise into double distilled water (50 mL) at room temperature under continuous stirring to form a white precipitate. The resulting white-colored precipitate was harvested by centrifugation, washed several times using double-distilled water and ethanol, and then dried in an oven at 80 °C over night to obtain the precursor In(OH)$_3$. This precursor was further calcined in air at 300°C for 2 h to obtain the In$_2$O$_3$ nanocubes. The color of the the precursor was changed from white to pale-yellow during calcination.

2.3 Characterization

X-ray diffraction (XRD) analysis was performed with a Bruker diffractometer (D8, Advance, Bruker AXS model) with CuK$_\alpha$ radiation ($\lambda$=1.5406 Å) operating at 40 kV and 40 mA. The transmission electron microscopy (TEM) images were recorded with a transmission electron microscope (HRTEM, Tecnai G$^2$ 20 Twin, FEI, USA) operating at an accelerating voltage of 200 kV. The FTIR spectroscopy analysis was carried out using FTIR spectrometer (FTIR-4800, Shimadzu, Japan) by the conventional KBr method in the spectral range 4000-400 cm$^{-1}$.

2.4 Gas Sensing Measurements

The In$_2$O$_3$ powder was pressed into pellets under a pressure of 15 MPa and the ohmic contacts were made with the help of silver paste to form the sensing element. The gas sensing measurements were carried out on these sensing elements in a static gas chamber to sense hydrogen in air ambient. The sensing element was kept directly on a heater in the gas chamber and the temperature was varied from 50 to 400 °C. The temperature of the sensing element was monitored by chromel-alumel thermocouple placed in contact with the sensor. The known volume of the H$_2$ was introduced into the gas chamber pre-filled with air and it was maintained at atmospheric pressure. The electrical resistance of the sensing element was measured before and after exposure to hydrogen using a sensitive digital multimeter (2000, Digital Multimeter, Keithley, U.S.A) controlled by a personal computer. The performance of the sensing element is presented in terms of gas response (S), which is defined as:

$$S = \frac{R_{\text{air}}}{R_{\text{gas}}}$$

where $R_{\text{air}}$ and $R_{\text{gas}}$ are the electrical resistance values of the sensor element in air and in the presence of H$_2$, respectively.

3. Results and Discussion

3.1 Structural and morphological characteristics

The XRD pattern of the calcined product is shown in Fig.1(a). It exhibits the diffraction peaks at 20 values of 29.78°, 31.16°, 34.52°, 44.99°, 50.24°, 57.11° and 59.63°, which are attributed to the formation of cubic phase of In$_2$O$_3$ (JCPDS No. 01-073-6440). No other peaks were observed, indicating that no impurities were present and confirming that the adopted synthesis method gives pure In$_2$O$_3$.

The FTIR spectrum of the calcined product is shown in Fig.1(b). It shows the bands at approximately 424, 561 and 603 cm$^{-1}$ (inset of Fig.1(b)) corresponding to the cubic In$_2$O$_3$ phase. The bands at 424 and 561 cm$^{-1}$ are attributed to In–O stretching whereas the band at 603 cm$^{-1}$ is a characteristic of In–O bending vibrations in the cubic In$_2$O$_3$.[23, 24] In addition, the broad band at ~3450 cm$^{-1}$ may be assigned to the stretching vibrational mode of an O-H group bonded to the In atom, i.e., In-OH.[24] Thus, FTIR spectroscopy result reveals that the phase formation is complete for the as-synthesized In$_2$O$_3$ nanocubes and there is no evidence for the presence of any byproduct (s) in the sample.

The surface morphologies of the calcined product [Fig.1(c)] reveals the formation In$_2$O$_3$ nanocubes with a typical edge length of ~25 nm. The corresponding selected area electron diffraction (SAED) pattern [Fig.1(d)] further confirms the random orientations of the In$_2$O$_3$ nanocubes and that no secondary phase exists.

3.2 H$_2$ sensing Characteristics

To evaluate the potential applicability of as-prepared In$_2$O$_3$ nanocubes in gas sensing applications, their H$_2$ sensing properties were investigated. It is well known that for metal oxide gas sensors, the operating temperature is an important factor and the response of the gas sensor exhibits a maximum value at a certain operating temperature. In order to determine the optimum operating temperature for H$_2$ gas detection, the response of as-prepared In$_2$O$_3$ nanocubes to 50 ppm H$_2$ was initially measured over an operating temperature range of 150–350 °C. Before exposing to the H$_2$ gas, the sensing element was allowed to equilibrate inside the gas chamber at...
The reproducibility and stability are important parameters to be considered when evaluating the performance of gas sensors. It is useful to have both a stable base line resistance and a reproducible signal change to a given analyte concentration. The reproducibility and stability of the In$_2$O$_3$ nanocubes were measured by repeating the test three times. The gas response values are maintained and the recovery abilities are not reduced after several sensing cycles. Thus, the In$_2$O$_3$ nanocubes exhibit a stable and reproducible characteristic, which suggests that it can be used as a reusable sensing material for the detection of H$_2$ gas.

The gas response of the as-prepared In$_2$O$_3$ nanocubes as a function of H$_2$ gas concentration at an operating temperature of 325°C is shown in Fig.2(c). The gas response increases approximately linearly as the H$_2$ concentration increases from 5 to 60 ppm. The linear relationship between the gas response and that of the H$_2$ concentration can be expressed as

$$y = 12.99 + 1.99x, R = 0.9967 \quad (2)$$

where $x$, $y$, and $R$ represent the H$_2$ concentration, gas response and correlation coefficient, respectively. The broken lines in the Fig.2(c) indicate the linear fit to the experimental data, illustrating the good quality of the fit. The linearity of the gas response suggests that the In$_2$O$_3$ nanocubes can be reliably used to monitor the concentration of H$_2$ over this range. Selectivity is an important parameter of gas sensors and it is the ability of a sensor to respond to a certain gas in presence of other gases. Theoretically, the sensors should have high response to some gases and little or no response to other gases in the same surroundings. The H$_2$ sensing selectivity of the In$_2$O$_3$ nanocubes is examined towards various gases such as liquid petroleum gas (LPG), carbon monoxide (CO), carbon dioxide (CO$_2$) and ethanol (C$_2$H$_5$OH) at 50 ppm and 325°C. The responses to each gas were calculated by equation (1). The responses to each gas were calculated by equation (1).

$$K = \frac{S_{H2}}{S_B} \quad \ldots \ldots \ldots (3)$$

where $S_{H2}$ and $S_B$ are the responses of sensors to H$_2$ and B gas, respectively. The selectivity coefficients for the In$_2$O$_3$ nanocubes were 99.21 to CO$_2$, 93.38 to CO, 40.70 to NH$_3$, 18.43 to ethanol, 6.85 to acetone and 3.21 to LPG. Commonly, the selectivity coefficient of sensors should be more than 5. Thus, the experimental results indicate that the In$_2$O$_3$ nanocubes based sensor has a good selectivity to H$_2$. Based on the observed results, it can be concluded that the formation of In$_2$O$_3$ nanocubes is not only effective in enhancing the H$_2$ response but also in making it selective for the detection of H$_2$.

4. Conclusions

In summary, we reported a highly selective and fast-responding H$_2$ sensor based on In$_2$O$_3$ nanocubes synthesized via a wet chemical route at room temperature. The gas sensing measurements reveal that the sensor based on the In$_2$O$_3$ nanocubes exhibit higher response (~ 127 to 50 ppm H$_2$ gas at 325°C), response time (~1-2 s), recovery time (~4-5 s), excellent reproducibility, good sensing selectivity, and lower detection limit (~3.87 ppm H$_2$ < PEL) and relatively lower operating temperature (~325°C). This work demonstrates the potential of using In$_2$O$_3$ nanocubes as sensing material in the fabrication of H$_2$ sensors.
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References


Figure 1: (a) XRD pattern, (b) FTIR spectrum, (c) TEM image and (d) the corresponding SAED pattern of as-synthesized In₂O₃ nanocubes.

Figure 2: (a) Graph showing the gas response as a function of operating temperature and (b) graph showing the gas response as a function of time with fluctuations.
Figure 2: (a) Effect of operating temperature on the gas response of In$_2$O$_3$ nanocubes to 50 ppm H$_2$ gas, (b) Response and recovery characteristics of In$_2$O$_3$ nanocubes to 50 ppm H$_2$ gas at 325°C (Inset depicts the repetitive response to 50 ppm H$_2$ gas at 325°C), (c) Gas response of In$_2$O$_3$ nanocubes as a function of H$_2$ concentration at 325°C and (d) Bar chart showing the gas response of In$_2$O$_3$ nanocubes for different gases. The gas concentration and operating temperature in all cases were 50 ppm and 325°C, respectively.