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$_4$OH as 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 (1 s), fast recovery (4–5 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 candidature 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 highly sensitive material for the detection of both reducing and oxidizing gases [19]. Few research groups have recently reported H$_2$ sensors based on pure In$_2$O$_3$ nanostructures with different morphologies [21, 22]. Qureshi 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 catalysed 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 ºC, 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 rate (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, rinsed several times using double-distilled water and ethanol, and then dried in an oven at 80 ºC 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 G20 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 ºC. 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$_2$ gas, 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 29.78º, 31.16º, 34.52º, 44.99º, 50.24º, 57.11º and 59.63º, 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 ºC. Before exposing to the H$_2$ gas, the sensing element was allowed to equilibrate inside the gas chamber at
an operating temperature for 1 h. A number of experiments have been carried out to measure the gas response as a function of the operating temperature. All the time the gas response of the sensor element has approximately constant values, indicating good repeatability of the sensor. The gas response of the as-prepared In$_2$O$_3$ nanocubes to 50 ppm H$_2$ as a function of operating temperature is shown in Fig.2(a). At low temperatures, the gas response is relatively low (e.g. S = 1.1 at 150 °C), but it increases rapidly with an increase in the operating temperature. The gas response attains a maximum at ~ 325°C (S ~127) and thereafter it decreases with a further increase of the operating temperature. Thus, the optimum operating temperature for the In$_2$O$_3$ nanocubes to detect H$_2$ was at 325°C, which is the modest from the viewpoint of semiconducting oxide gas sensors. Hence, 325°C is the optimum operating temperature in this work and further gas sensing experiments were performed at this temperature.

The reproducibility and stability are important parameters to evaluate the performance of gas sensors. The response time is defined as the time required by the sensor to reach 90% of the full response, whereas recovery time is the time required to reach the 10% of the sensor baseline resistance. The response and recovery characteristics of the In$_2$O$_3$ nanocubes to 50 ppm H$_2$-gas at 325°C is shown in Fig.2(b). Five samples were tested from each batch and each sample was tested three times. It was observed that the response of the sensor increases when exposed to the H$_2$ (reducing gas) gas, which suggests that In$_2$O$_3$ nanocubes behaves as a n-type semiconductor. As can be seen from Fig.2(b), the sensor responds rapidly after introduction of H$_2$ gas and recovers immediately when it is exposed to air. The In$_2$O$_3$ nanocubes has response time of ~ 1-2 s and the recovery time of ~ 4-5 s.

The reproducibility and stability are important parameters to be considered when evaluating the performance of a sensor. It is useful to have both a stable baseline resistance and a reproducible signal change to a given analyte concentration. The reproducibility and stability of the In$_2$O$_3$ nanocubes gas were measured by repeating the test three times. The gas response of the In$_2$O$_3$ nanocubes upon periodic exposure to 50 ppm H$_2$ gas at 325°C is shown in inset of Fig.2(b). The In$_2$O$_3$ nanocubes show good reproducibility upon repeated exposure and removal of H$_2$ under same conditions. Furthermore, the repeated tests revealed that 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

$$y = 12.99 + 1.99x, R = 0.9967$$  \hspace{1cm} (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. Detection limit is another important factor used for the evaluation of the sensing-performance of the sensors. It is defined as the lowest concentration of the analyte at which the response of the sensor under the given conditions is differentiated from the background level. When this criterion is applied in the present work the H$_2$ response was set to $S > 7.71$. According to the equation (2), the detection limit is estimated to be approximately 3.87 ppm for the sensor based on as-prepared In$_2$O$_3$ nanocubes. The permissible exposure limit (PEL) for H$_2$ as specified by National Institute for Occupational Safety and Health (NIOSH) is 4 ppm. In this work, the detection limit for In$_2$O$_3$ nanocubes is ~ 3.87 ppm which is lower than the PEL for H$_2$.

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). Fig. 2(d) depicts the histogram of the responses of the sensor based on In$_2$O$_3$ nanocubes toward 50 ppm of LPG, H$_2$, CO, CO$_2$ and ethanol at 325 °C. The In$_2$O$_3$ nanocubes exhibit higher response to H$_2$ (127), whereas it shows a considerably lower response (~39.54) to LPG, CO, CO$_2$ and ethanol. The selectivity coefficient (K) of H$_2$ to another gas is defined as [25]:

$$K = \frac{S_{H_2}}{S_B} \hspace{1cm} \text{(3)}$$

where $S_{H_2}$ and $S_B$ are the responses of sensors in 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 In$_2$O$_3$ nanocubes.
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.