

A Highly Selective and Fast-Responding Hydrogen Sensor based on In₂O₃ Nanocubes

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Abstract: The In₂O₃ nanocubes were successfully synthesized without any templates by calcining the In(OH)₃ precursor in air at 300 °C for 2 h and their H₂ sensing characteristics were investigated. The In(OH)₃ precursor was prepared through a wet chemical route at room temperature (27 °C) using InCl₃, 4H₂O and NH₄OH as starting materials. The formation of In₂O₃ nanocubes was confirmed by X-ray diffraction measurement (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) analysis. The In₂O₃ nanocubes exhibit excellent H₂ sensing properties such as, high gas response (~130 to 50 ppm H₂ at 325 °C), extremely rapid response (1s), 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 H₂. The experimental results demonstrate the potential of the In₂O₃ nanocubes as sensing material in the fabrication of hydrogen sensors.

Keywords: In₂O₃ nanocubes, H₂ sensor, Semiconductor gas sensors, TEM, XRD.

1. Introduction

Hydrogen (H₂) 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 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 cm²/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. Aroutiounian [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 H₂ sensor based on ZnSnO₃ cubic crystallites

synthesized by a hydrothermal method. Amongst other recent studies, Katoch et al [11] have reported SnO₂-ZnO nano fiber composite for drastically enhancing the sensing behavior H₂ gas and Wang et al [12] report a low temperature, high performance hydrogen gas sensors using palladium decorated tungsten oxide.

Indium oxide (In₂O₃) 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]. In₂O₃, as an 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 H₂ sensors based on pure In₂O₃ nanostructures with different morphologies [21, 22]. Qurashi et al [20] reported the H₂ sensor based on In₂O₃ nano wires (~70 nm) and nano needles (150-200 nm) synthesized via catalyst supported growth by vapor transport. The In₂O₃ 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 H₂ 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 In₂O₃ nano towers with an octahedral cap size of 600 nm synthesized via thermal evaporation of In₂O₃ and active carbon powders. The In₂O₃ nano towers showed a high response of 83 % towards 1000 ppm of H₂ at 240 °C with a response time of 63 s. The detailed study on the influence of morphology of In₂O₃ on the H₂ gas sensing properties was reported recently by Shanmugasundaram et al [22]. These authors prepared the In₂O₃ 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_2O_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_2O_3 cubic crystallites. In this study, the In_2O_3 cubic crystallites were synthesized through a wet chemical route at room temperature. Sensing characteristics of the In_2O_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 tetrahydrate ($\text{InCl}_3 \cdot 4\text{H}_2\text{O}$) 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_2O_3 nanocubes

In a typical synthesis of In_2O_3 nanocubes, 0.29 g of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ was dissolved in 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 overnight to obtain the precursor $\text{In}(\text{OH})_3$. This precursor was further calcined in air at 300 °C for 2 h to obtain the In_2O_3 nanocubes. The color of 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_α radiation ($\lambda=1.5406 \text{ \AA}$) operating at 40 kV and 40 mA. The transmission electron microscopy (TEM) images were recorded with a transmission electron microscope (HRTEM, Tecnai G² 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_2O_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 :

$$S = \frac{R_{\text{air}}}{R_{\text{gas}}} \quad (1)$$

where R_{air} and R_{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 2θ 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_2O_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_2O_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_2O_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_2O_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_2O_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 of In_2O_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_2O_3 nanocubes and that no secondary phase exists.

3.2 H_2 sensing Characteristics

To evaluate the potential applicability of as-prepared In_2O_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_2O_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

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 In₂O₃ nanocubes to 50 ppm H₂ 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 In₂O₃ nanocubes to detect H₂ 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 response and recovery times are also important parameters for evaluating 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 In₂O₃ nanocubes to 50 ppm H₂ 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 H₂ (reducing gas) gas, which suggests that In₂O₃ nanocubes behaves as a n-type semiconductor. As can be seen from Fig.2(b), the sensor responds rapidly after introduction of H₂ gas and recovers immediately when it is exposed to air. The In₂O₃ 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 base line resistance and a reproducible signal change to a given analyte concentration. The reproducibility and stability of the In₂O₃ nanocubes gas were measured by repeating the test three times. The gas response of the In₂O₃ nanocubes upon periodic exposure to 50 ppm H₂ gas at 325°C is shown in inset of Fig.2(b). The In₂O₃ nanocubes show good reproducibility upon repeated exposure and removal of H₂ 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 In₂O₃ nanocubes exhibit a stable and reproducible characteristic, which suggests that it can be used as a reusable sensing material for the detection of H₂ gas.

The gas response of the as-prepared In₂O₃ nanocubes as a function of H₂ gas concentration at an operating temperature of 325°C is shown in Fig.2(c). The gas response increases approximately linearly as the H₂ concentration increases from 5 to 60 ppm. The linear relationship between the gas response and that of the H₂ concentration can be expressed as

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

where **x**, **y** and **R** represent the H₂ 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 In₂O₃ nanocubes can be reliably used to monitor the concentration of H₂ 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 H₂ 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 In₂O₃ nanocubes. The permissible exposure limit (PEL) for H₂ as specified by National Institute for Occupational Safety and Health (NIOSH) is 4 ppm. In this work, the detection limit for In₂O₃ nanocubes is ~ 3.87 ppm which is lower than the PEL for H₂.

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 H₂ sensing selectivity of the In₂O₃ nanocubes is examined towards various gases such as liquid petroleum gas (LPG), carbon monoxide (CO), carbon dioxide (CO₂) and ethanol (C₂H₅OH) 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 In₂O₃ nanocubes toward 50 ppm of LPG, H₂, CO, CO₂ and ethanol at 325 °C. The In₂O₃ nanocubes exhibit higher response to H₂ (127), whereas it shows a considerably lower response (<39.54) to LPG, CO, CO₂ and ethanol. The selectivity coefficient (K) of H₂ to another gas is defined as [25]:

$$K = \frac{S_{H_2}}{S_B} \quad \dots \dots \dots (3)$$

where S_{H₂} and S_B are the responses of sensors in H₂ and B gas, respectively. The selectivity coefficients for the In₂O₃ nanocubes were 99.21 to CO₂, 93.38 to CO, 40.70 to NH₃, 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 In₂O₃ nanocubes based sensor has a good selectivity to H₂. Based on the observed results, it can be concluded that the formation of In₂O₃ nanocubes is not only effective in enhancing the H₂ response but also in making it selective for the detection of H₂.

4. Conclusions

In summary, we reported a highly selective and fast-responding H₂ sensor based on In₂O₃ nanocubes synthesized via a wet chemical route at room temperature. The gas sensing measurements reveal that the sensor based on the In₂O₃ nanocubes exhibit higher response (~ 127 to 50 ppm H₂ 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 H₂ < PEL) and relatively lower operating temperature (~ 325°C). This work demonstrates the potential of using In₂O₃ nanocubes as sensing material in the fabrication of H₂ sensors.

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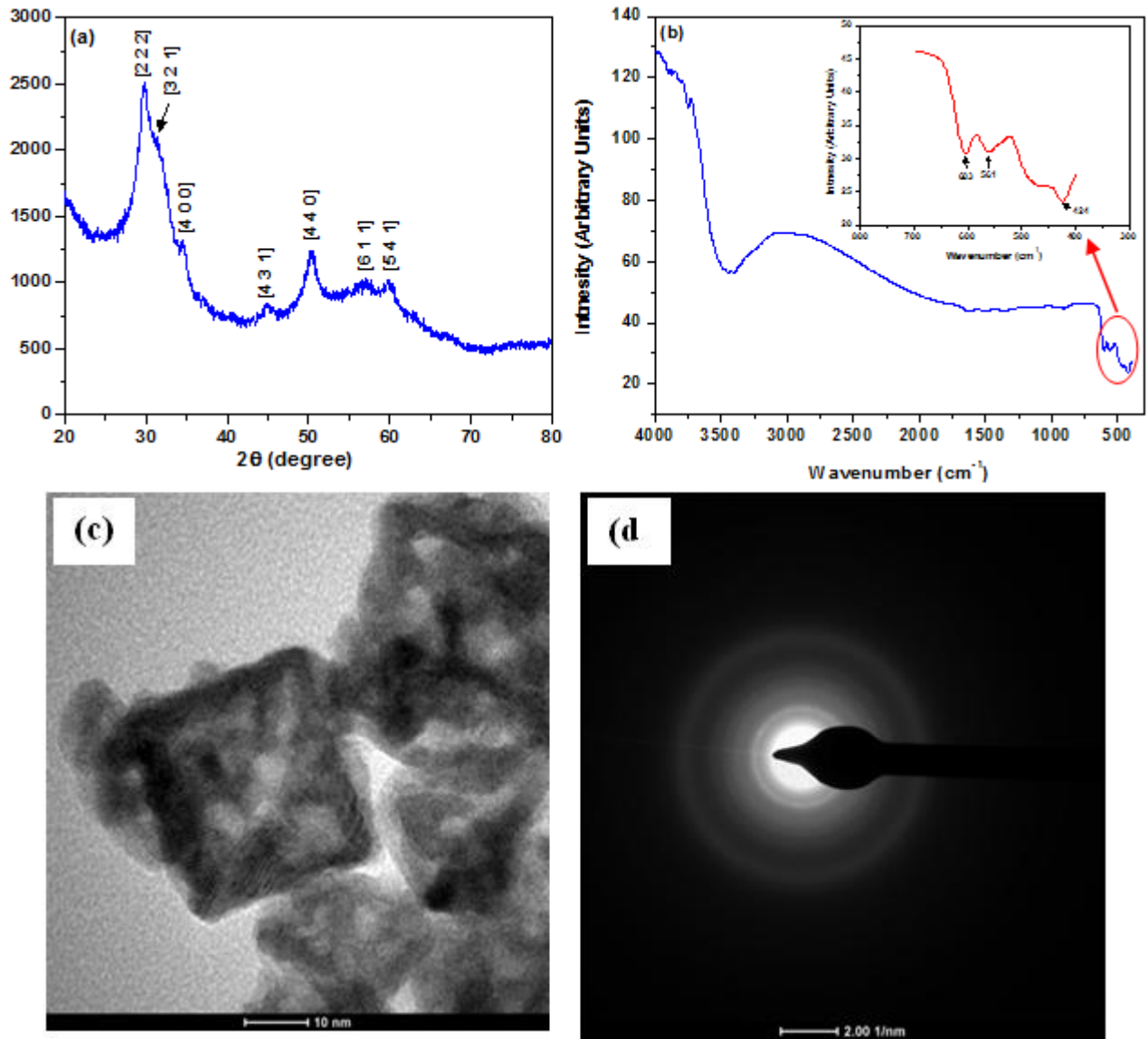
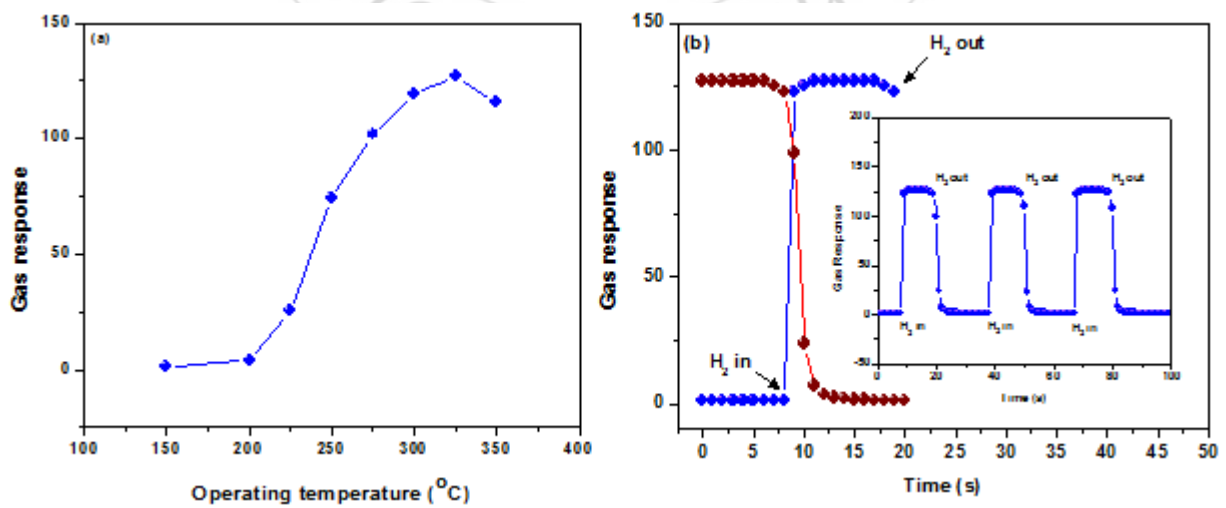


Figure 1: (a) XRD pattern, (b) FTIR spectrum, (c) TEM image and (d) the corresponding SAED pattern of as-synthesized In₂O₃ nanocubes.



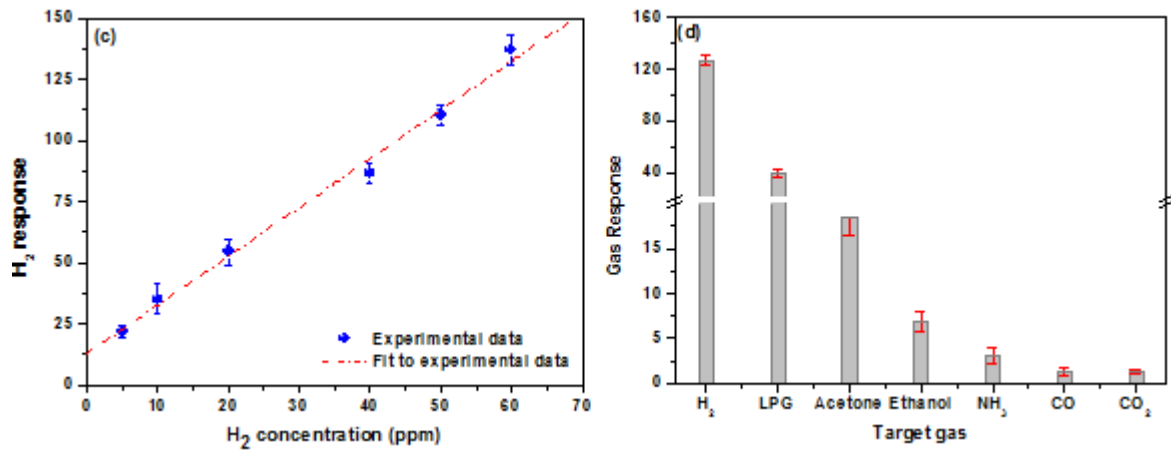


Figure 2: (a) Effect of operating temperature on the gas response of In₂O₃nanocubes to 50 ppm H₂ gas, (b) Response and recovery characteristics of In₂O₃nanocubes to 50 ppm H₂ gas at 325°C (Inset depicts the repetitive response to 50 ppm H₂ gas at 325°C), (c) Gas response of In₂O₃nanocubes as a function of H₂ concentration at 325 °C and (d) Bar chart showing the gas response of In₂O₃nanocubes for different gases. The gas concentration and operating temperature in all cases were 50 ppm and 325°C, respectively.

