International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2013): 6.14 | Impact Factor (2014): 5.611

A Highly Selective and Fast-Responding Hydrogen Sensor based on In_2O_3 Nanocubes

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Abstract: ***The In_2O_3 nanocubeswere 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 $InCl_3$,$4H_2O$ and NH_4OHas starting materials.The formation ofIn_2O_3 nanocubes was confirmed by X-ray diffraction measurement (XRD), X-ray photoelectron spectroscopy (XPS)and transmission electron microscopy (TEM)analysis.The In_2O_3 nanocubes exhibit excellentH_2 sensing properties such as, high gas response (~130 to 50 ppm H_2 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 H_2. The experimental results demonstrate the potential of theIn_2O_3 nanocubes as sensing material in the fabrication of hydrogen sensors.***

Keywords: In_2O_3nanocubes, H_2sensor, 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 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 is 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. Aroutiounian [9]has reviewed, complied 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] al 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_2O_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].Ithas 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_2O_3, 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 H_2 sensors based on pure In_2O_3 nanostructures with different morphologies [21, 22]. Qurashi et. al [20] reported the H_2 sensor based on In_2O_3 nano wires (~70 nm) and nano needles (150-200 nm) synthesized via catalyst supported growth by vapor transport. The In_2O_3nanowires 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_2O_3 nano towers with an octahedral cap size of 600 nm synthesized via thermal evaporation of In_2O_3 and active carbon powders. The In_2O_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_2O_3 on the H_2 gas sensing properties was reported recently by Shanmugasundaram et. al [22]. These authors prepared the In_2O_3having different morphologies like nanobricks(200 nm × 200 nm × 50 nm) nano particles (10−20 nm), mesoporous nannocubes (200 nm × 200 nm × 200 nm) and nanoflakes by using a facile hydrothermal route. This study unambiguously demonstrated thatthe 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 ^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_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_3cubic crystallites to H_2were systematically investigated. A sensing mechanism is also discussed based on experimental findings.

2. Experimental

2.1 Materials

All of the chemicals were of analytical gradeand were used as-received without any further purification. The indium chloride tetrahyd rate ($InCl_3$, $4H_2O$) 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 typicalsynthesis of In_2O_3 nanocubes, 0.29 g of $InCl_3$,$4H_2O$ 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 ^{o}Cover night to obtain the precursor $In(OH)_3$. This precursor was further calcined in air at 300 ^{o}C for 2 h to obtain theIn_2O_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_α radiation (λ=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

TheIn_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 ^{o}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 :

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

where R_{air} and R_{gas} are the electrical resistance values of the sensor element in air and in the presence of H_2gas, respectively.

3. Results and Discussion

3.1 Structural and morphological characteristics

The XRD pattern of the calcinied product is shown in Fig.1(a). It exhibits the diffraction peaks at 2θ values of 29.78^o, 31.16^o, 34.52^o, 44.99^o, 50.24^o, 57.11^o and 59.63^o, 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 calcinied 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–Ostretching 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 calcinied product [Fig.1(c)] reveals the formation 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_2sensing Characteristics

To evaluate the potential applicability of as-prepared In_2O_3 nanocubesin gas sensing applications, theirH_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_2gas 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 ^{o}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 In_2O_3 nanocubes to 50 ppm H_2as 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 ^oC), but it increases rapidly with an increase in the operating temperature. The gas response attains a maximum at ~ 325^oC (S ~127) and thereafter it decreases with a further increase of the operating temperature. Thus, the optimum operating temperature for the In_2O_3 nanocubes to detect H_2 was at 325^oC, which is the modest from the viewpoint of semiconducting oxide gas sensors. Hence, 325^oC 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 In_2O_3 nanocubes to 50 ppmH_2gas at 325^oC 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_2O_3 nanocubes behaves as a n-type semiconductor. As can be seen from Fig.2(b), the sensor responds rapidly after introduction of H_2gas and recovers immediately when it is exposed to air. The In_2O_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 base line resistance and a reproducible signal change to a given analyte concentration. The reproducibility and stability of the In_2O_3 nanocubes gas were measured by repeating the test three times. The gas response of the In_2O_3 nanocubes upon periodic exposure to 50 ppm H_2 gas at 325^oC is shown in inset of Fig.2(b). The In_2O_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_2O_3 nanocubes exhibit a stable and reproducible characteristic, which suggests that itcan be used as a reusable sensing material for the detection of H_2 gas.

The gas response of the as-preparedIn_2O_3 nanocubes as a function of H_2 gas concentration at an operating temperature of 325^oC 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

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

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_2O_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_2response 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-preparedIn_2O_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_2O_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 othergases. 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_2O_3 nanocubes is examined towards various gases such as liquid petroleum gas (LPG),carbon monoxide (CO), carbon dioxide (CO_2) and ethanol (C_2H_5OH) at 50 ppm and 325 ^oC. 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_2O_3 nanocubes toward 50 ppm of LPG, H_2, CO, CO_2 and ethanol at 325 ^oC. The In_2O_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]:

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

where S_{H2} and S_B are the responses of sensors in H_2 and B gas, respectively. The selectivity coefficients for the In_2O_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 and3.21 to LPG, Commonly, the selectivity coefficient of sensors should be more than 5. Thus, the experimental results indicate that the In_2O_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_2O_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_2O_3nanocubes synthesized via a wet chemical route at room temperature. The gas sensing measurements reveal that the sensor based on the In_2O_3nanocubes exhibit higher response (~ 127 to 50 ppm H_2 gas at 325^oC), 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^oC).This work demonstrates the potential of using In_2O_3nanocubes as sensing material in the fabrication of H_2 sensors.

5. Acknowledgement

The authors acknowledge financial support from University Grants Commission (UGC), New Delhi (Project No. F. 530/2/DRS/2010 -SAP-DRS, Phase-II). One of us (SST) is thankful to North Maharashtra University, Jalgaon for providing financial support through the VCRMS Scheme.

References

[1] G. Haoshuang, W. Zhao and H. Yongming, Hydrogen gas sensors based on semi conductoroxide nanostructures, *Sensors,*2012, **12**, 5517-5550.
[2] S. Verhelst, R. Sierens, Hydrogen engine-specific properties,*Int. J. Hydrogen Energy,*2001, **26**, 987–990.
[3] T. Hübert, L. Boon-Brett, G. Black and U. Banach, Hydrogen sensors—A review,*Sens. Actuat., B* 2011, **157**, 329–352.
[4] W. J. Buttner, M. B. Post, R. Burgess and C. Rivkin, An overview of hydrogen safety sensors and requirements, *Int. J. Hydrog. Energy,* 2011, **36**, 2462–2470.
[5] V. Aroutiounian, Hydrogen detectors, *Int. Sci. J. Altern. Energy Ecol.,* 2005, **3**, 21–31.
[6] Y. Wang, B. Liu, S. Xiao, H. Li, L. Wang, D. Cai, D. Wang, Y. Liu, Q. Li and T. Wang, High performance and negative temperature coefficient of low temperature hydrogen gassensors using palladium decorated tungsten oxide,*J. Mater. Chem. A*2015, **3**, 1317–1324.
[7] N. H. Al-Hardan, M. J. Abdullah,A. A. Aziz, Sensing mechanism of hydrogen gas sensor based on RF-sputtered ZnO thin films, *Int. J.Hydrogen Energy,* 2010, **35**, 4428-4434.
[8] S. Sumida, S. Okazaki, S. Asakura, H. Nakagawa,H. Murayama and T. Hasegawa,Distributed hydrogen determination with fiber-optic sensor,*Sens. Actuators B*, 2005,**108**, 508–514.
[9] V. Aroutiounian, Metal oxide hydrogen, oxygen and carbon monoxide sensors for hydrogen setups and cells, *Int. J. Hydrogen Energy*, 2007,**32**,1145-1158.
[10] P. Wadkar, D. Bauskar, P. Patil, High performance H_2 sensor based on$ZnSnO_3$ cubic crystallites synthesized by a hydrothermal method, *Talanta*,2013, **105**, 327-332.
[11] A. Katoch, K. Jae-Hun,J. K. Yong,W. K. Hyoun and S. K.Sang, Bifunctional sensing mechanism of SnO_2−ZnO composite nano fibers for drastically enhancing the sensing behavior in H_2 gas, *ACS Appl. Mater. Interfaces,*2015,**7**, 11351−11358.
[12] Y. Wang, B. Liu, S. Xiao, H. Li, L. Wang, D. Cai,D. Wang,Y. Liu, Q. Li, T. Wang,High performance and negative temperature coefficient of low temperature hydrogen gassensors using palladium decorated tungsten oxide, *J. Mater. Chem. A,*2015, **3**, 1317–1324.
[13] C. Y. Huang, G. C. Lin, Y. J. Wu, T. Y. Lin, Y. J. Yang and Y. F. Chen, Efficient light harvesting by well-aligned In_2O_3nanopushpins as antireflection layer on Si solar cells, *J. Phys. Chem. C,* 2011, **115**, 13083−13087.
[14] J. Parrondo, R. Santhanam, F. Mijangos and B. Rambabu, Electrocatalytic performance of In_2O_3-supported Pt/C nanoparticles for ethanol electro-oxidation in direct ethanol fuel cells, *Int. J. Electrochem. Sci*., 2010, **5**,1342-1354.
[15] W. H. Ho, C. F. Li, H. C. Liu, S. K.Yen, Electrochemical performance of In_2O_3thin film electrode in lithium cell, *J. Power Sources*,2008, **175**, 897−902.
[16] D. Zhang, Z. Liu, C. Li,T. Tang,X. Liu, S. Han, B. Lei and C. Zhou, Detection of NO_2 down to ppb Levels using Individual and Multiple In_2O_3 Nanowire Devices,*Nano Lett*.,**2004**, *4*, 1919-1923.
[17] P.Nguyen,H.T.Ng,T.Yamada,M. K. Smith, J.Li, J.Han and M.Meyyappan,Direct integration of metal oxide nanowire in vertical field-effect transistor,*Nano Lett*.,**2004**, 4, 651-657.
[18] J.Cui, A.Wang, N. L.Edleman, J.Ni, P.Lee, N. R.Armstrong and T. J. Marks, Indium tin oxide alternatives-high work function transparent conducting oxides as anodes for organic light-emitting diodes,*Adv. Mater.*,**2001**, *13*, 1476-1480.
[19] X. J. Huang and Y. K.Choi, Chemical sensors based on nanostructured materials, *Sens. Actuators B,* **2007**, 122 659–671.
[20] A.Qurashi,E. M.Maghraby, T. Yamazaki and T.Kikuta, Catalyst supported growth of In_2O_3 nanostructures and their hydrogen gas sensing properties,*Sens. Actuators B,***2010**, 147, 48–54.
[21] Z. Q.Zheng, L. F.Zhu and B.Wang, In_2O_3Nanotower hydrogen gas sensors based on both schottky junction and thermoelectronic emission,*Nano. Res. Letts*.,**2015**, 10, 293-307.
[22] A.Shanmugasundaram, B.Ramireddy,P.Basak,S. V.Manorama and S.Srinath, Hierarchical $In(OH)_3$ as a precursor to mesoporousIn_2O_3nanocubes:A facile synthesis route, mechanism of self-assembly and enhanced sensing response toward hydrogen.,*J. Phys. Chem. C,***2014**, 118, 6909−6921.
[23] E. C. C.Souza, J. F. Q. Rey and E. N. S. Muccillo, Synthesis and characterization of spherical and narrow size distribution indium oxide nanoparticles, *Appl. Surf. Sci*.,**2009**, 255, 3779-3783.
[24] A.Ayeshamariam, M.Bououdina and C. Sanjeeviraja, Optical, electrical and sensing properties of In_2O_3 nanoparticles.,*Mater. Sci. Semiconductor Processing*,**2013**, 16, 686-695.
[25] M. Siemons and U. Simon, Gas sensing properties of volume-doped $CoTiO_3$ synthesized via polyol method, *Sens. Actuators B : Chemical*, **2007**, 126 595-603.

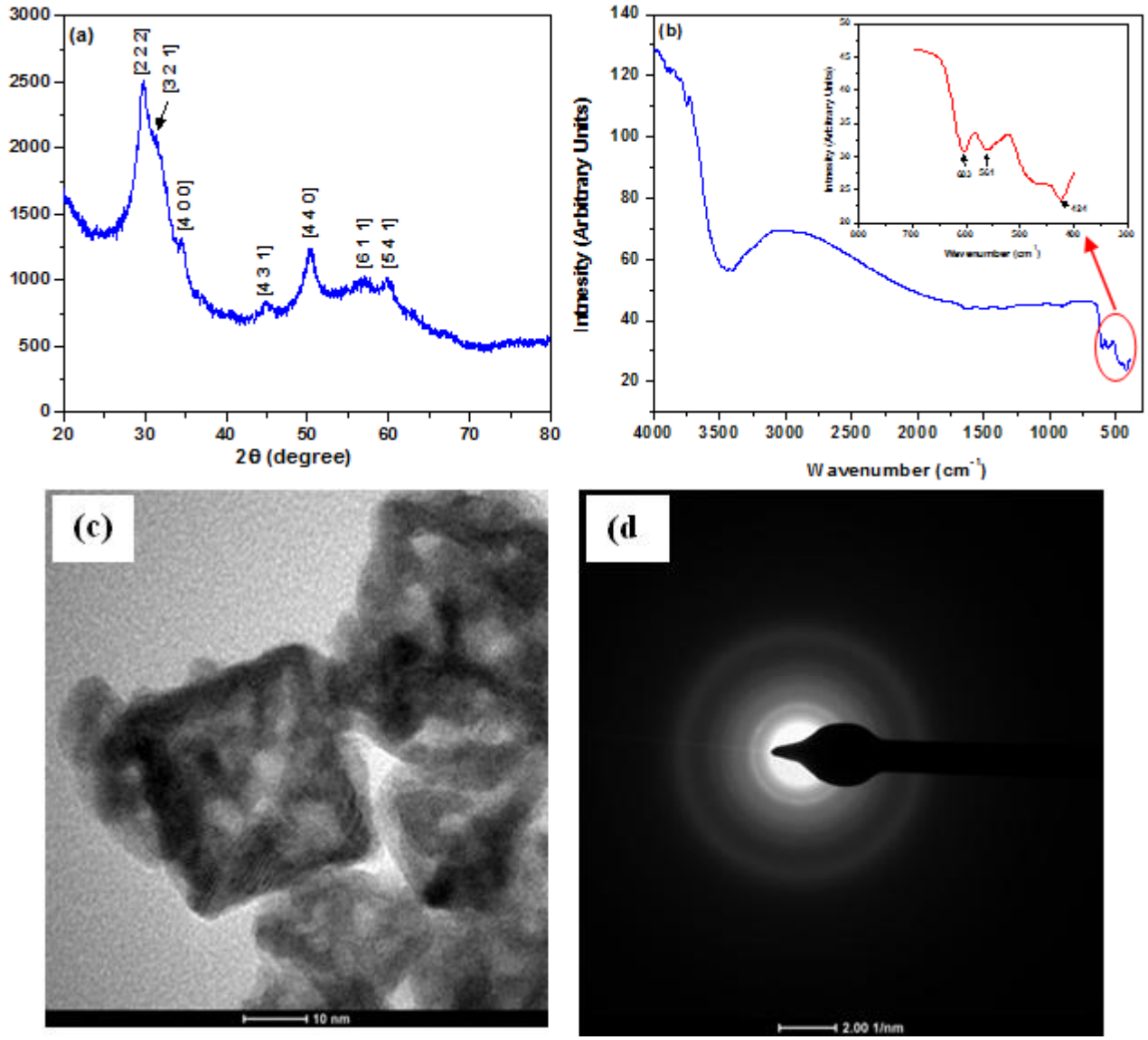
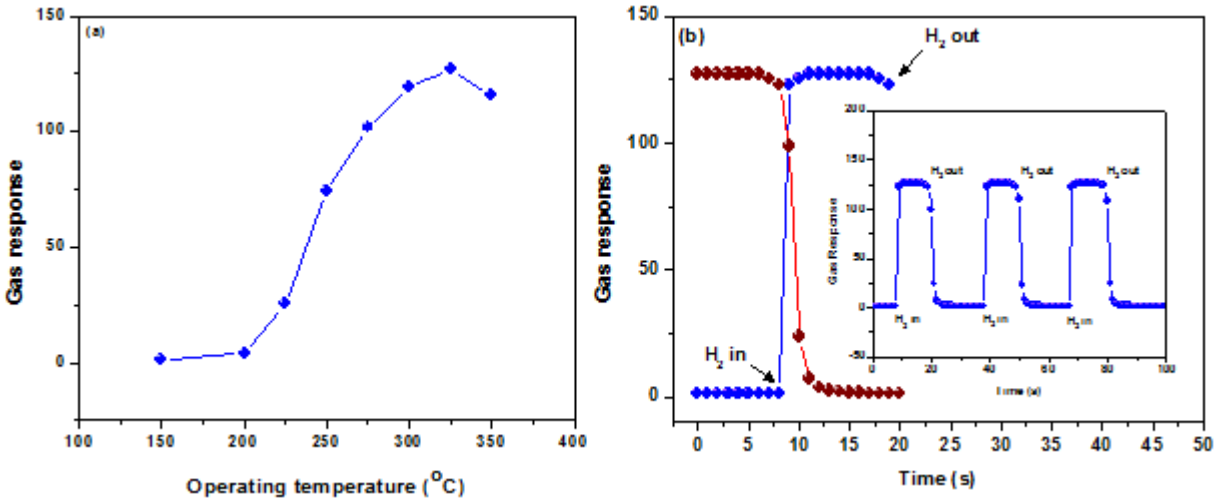


Figure 1: (a) XRD pattern, (b) FTIR spectrum, (c) TEM image and (d) the corresponding SAED pattern of as-synthesized In_2O_3nanocubes.



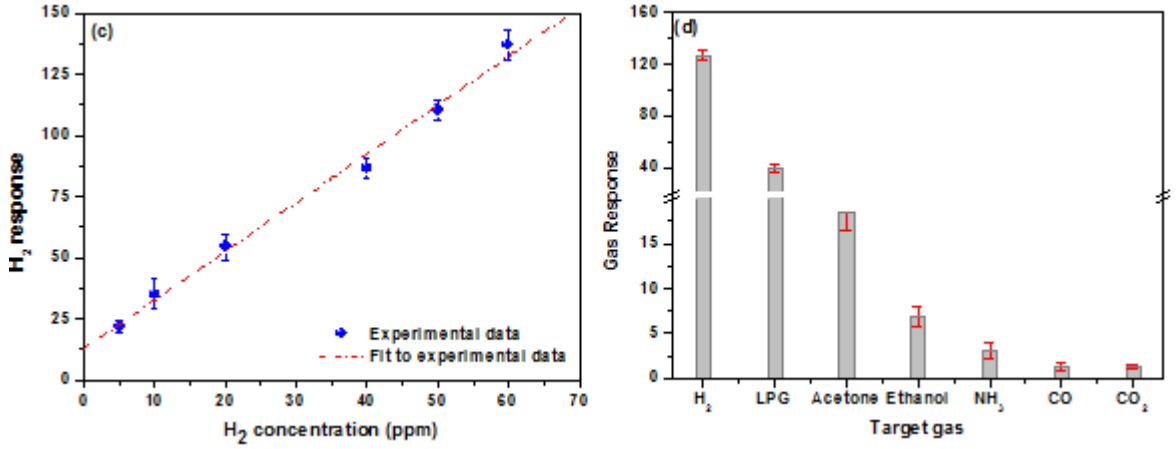


Figure 2: (a) Effect of operating temperature on the gas response of In_2O_3nanocubes to 50 ppm H_2 gas, (b) Response and recovery characteristics of In_2O_3nanocubes to 50 ppm H_2 gas at 325^oC (Inset depicts the repetitive response to 50 ppm H_2 gas at 325^oC), (c) Gas response of In_2O_3nanocubesas a function of H_2 concentration at 325 ^oC and (d) Bar chart showing the gas response of In_2O_3nanocubes for different gases. The gas concentration and operating temperature in all cases were 50 ppm and 325^oC, respectively.