Continuous hydrothermal flow-inspired synthesis and ultra-fast ammonia and humidity room-temperature sensor activities of WO₃ nanobricks

Shoyebmohamad F Shaikh 1, Balaji G Ghule 2, Pritamkumar V Shinde 3, Siddheshwar D Raut 2, Shyam K Gore 2, Mohd Ubaidullah 2, Rajaram S Mane 2,3,4 and Abdullah M Al-Enizi 1,4

1 Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia
2 School of Physical Sciences, Swami Ramanand Teerth Marathwada University, Nanded-431606, M.S., India
3 Global Frontier R&D Center for Hybrid Interface Materials, Pusan National University, 30 Jangjeon-Dong, Geumjung-Gu, Busan, Republic of Korea
4 Authors to whom any correspondence should be addressed. E-mail: rajarammane70@gmail.com and amenizi@ksu.edu.sa

Abstract

Mesoporous tungsten oxide nanobricks (WO₃ NBs) are successfully prepared via a simple and cost-effective hydrothermal synthesis method. The as-synthesized WO₃ NBs demonstrate a high sensitivity and selectivity when used for liquid ammonia and humidity sensor activities at room temperature (27 °C). The monoclinic crystal structure has been corroborated from x-ray diffraction studies and the specific surface area is estimated to be 38.74 m² g⁻¹. A larger specific surface area has significantly facilitated a fast gas adsorption/desorption process. The WO₃ NBs notably exhibit gas sensitivity and selectivity for volatile organic compounds (VOCs) such as ammonia; however, a moderate performance is displayed with different oxidizing and reducing agents at room-temperature, namely: toluene, methanol, ethanol, and acetone. The sensor has offered a commercial potential with an extremely high response (75%), a 15-day operational stability at 100 ppm concentration of ammonia, and a practically remarkable ultra-high 8/5 s response/recovery time. The WO₃ NBs-based humidity sensor endows a 32% resistance response at 20% relative humidity, with a quick response/recovery time of 10/8 s; which is due to unique surface architecture of these NBs.

Abbreviations

VOC volatile organic compound;
XRD x-ray diffraction

1. Introduction

Ammonia is being produced and applied extensively in various chemical production industries, medical diagnosis, fertilizer companies, and food plants, etc. Its leak during working atmosphere can result several health hazards problems on human working closely, like immediate burning of the nose, throat infection, lung related disease, irritating, and even burning the respiratory track [1]. The detection of ammonia, in its early stage, and the control of chemical pollution is urgent demand from the safety point of view. Since few years, several studies are focused to use metal oxides i.e. SnO₂, TiO₂, V₂O₅, MnO₂, ZnO, Bi₂O₃, MoO₃, MoO₃, NiO, and Co₃O₄, and several other combinations, that are capable to detect ammonia effectively with good sensitivity and selectivity [2]. Among these, WO₃ is a popular and least bothered an n-type semiconductor with promising electrochemical properties, a high surface area, a small pore-size distribution, with several exciting chemical and physical
properties, which have made it a appropriate material for various applications such as catalysts [3], gas sensors [4], and energy storage applications [5]. Up till, myriads of chemical and physical preparation methods like thermal evaporation, chemical vapor deposition, the sputtering, and colloidal suspension, have been applied for the synthesis of WO3 nanostructures of different phases and morphologies; nanoparticles, nanofiber, nanorods and nanowires [6, 7]. All reported synthesis methods could be either expensive, time consuming or tedious, with huge hazardous waste as toxic byproducts. Hydrothermal synthesis has received great consideration because of its simplicity, cost-effectiveness, soft chemical approach, low-temperature processing, and uniqueness in producing controlled shapes/sizes of various nanostructures [8, 9].

Siciliano et al reported a direct growth of WO3 film in an oxygen atmosphere using metal tungsten foil via a thermal evaporation method on a sapphire substrate which demonstrated a high sensitivity for NO2 gas, and less for NO and NH3 gases [10], Ciateanu et al used a pulsed laser deposition method of mediated crystalline WO3 films as oxygen gas detectors [11]. Zeng et al obtained porous WO3-based NO2 gas sensors using anodic oxidation of DC magnetron sputtering method onto an alumina substrate [12]. Surveying the literature in depth, it is inferred that the WO3 is a potential sensor material because of its large surface area and unique structural, optical, and electrical properties. However, WO3 as a sensor described in the literature has endowed its effective sensing operation above 150 °C; not in position of fabricating low-temperature operating sensor devices. Moreover, a high-temperature operation endows limited practical applications, viz., detection of flammable gases [13]. Several consecutive efforts have developed to reduce the operation temperature of these sensors likewise; the use of metal oxide-based gas sensors to detect various target gases at atmospheric temperature [14]. Teoh et al and Kim et al demonstrated WO3, room-temperature-based sensor that detected NO2 and NH3 gases with moderate values of response and recovery time [15, 16]. Moreover, above drawbacks might overcome by controlling the structure, morphology and surface area of WO3, prepared by soft-chemical methods.

In present study, a facile, simple and low-cost hydrothermal method is used to obtain WO3 NB gas sensors operating at room temperature. The WO3 NB gas sensors approve higher selectivity towards ammonia, than other VOCs such as ethanol, methanol, acetone, and toluene. The sensor for ammonia gas endows an ultra-fast response/recovery time. The schematic of gas sensing mechanism using a band structure change is closely analogous to experimental findings. The WO3 NBs gas sensor has also demonstrated remarkable sensing response for humidity.

2. Experimental details

2.1. Synthesis of WO3 NBs

The analytical grade ammonium paratungstate (NH4)10[3H2W12O42·4H2O, 99%], hydrochloric acid (HCl, 37%), and hydrogen peroxide (H2O2, 30% w/w in water) were used as received. In a facile synthesis process, 1 g of ammonium paratungstate was mixed in 95 ml distilled water (Milli-Q water; 18.2 MΩ cm) and concentrated HCl (~3 ml) and then stirred for a while. The stirring time was depending on the amount of HCl added. After the addition of nearly 2 ml of H2O2, the ammonium paratungstate solution initially turned to a transparent light yellow and then dark yellow by forming gelatinous precipitate, which was evidenced after continuously 1 h stirring to form transparent solution. A transparent solution was poured in a stainless-steel Teflon-lined autoclave. The hydrothermal synthesis reaction was conducted at a constant temperature of 160 °C for ~14 h (heating rate 5 °C min⁻¹). The whitish powder was taken off, rinsed with distilled water and calcinated at 500 °C for 1 h to increase the crystallinity of the as-obtained WO3 NBs (Scheme 1). The solid-state film was fabricated by taking 1 g of polyvinyl alcohol (PVA) in 10 ml of distilled water as a binder, which was kept at 90 °C while constant stirring until the solution became viscous. Then, a few drops of viscous PVA solution was mixed with the WO3 NBs in a pestle and mortar. This mixture was coated onto a soda-lime glass substrate and dried at 300 °C to vaporize the excess water and binder. The obtained film was used as a room-temperature gas and humidity sensor.

2.2. Characterization details

The optical transparency of WO3 NBs film was measured using a UV-visible spectrophotometer (V-530, Jasco, Japan). The DTA-TGA study measurement was carried out using a DSC-TGA standard instrument (SDT Q 600 v 20.9 Build 20). The surface morphology of the WO3 was confirmed from FE-SEM (Nova-SEM 200–FEI) digital silhouettes. The HR-TEM image was recorded using a FEI TECNAI G2 20 STWIN instrument. The x-ray diffraction (XRD) spectrum was used to investigate the crystal phase (XRD-6000, x-ray diffractometer, Shimadzu) with a Cu-Kα radiation tube. The x-ray photoelectron spectroscopy profile was acquired for determining the elemental composition via a PHI 5000 Versa Probe (Ulvac-PHI). Moreover, the BET surface-area and pore-size distribution analyses were measured on Belsorp II, BET, Japan Inc. instrument.
2.3. Gas sensor setup

The gas sensor performance was measured using 250 ml volume capacity stainless-steel chamber. PID-controlled heater was fixed at the base of the cylindrical chamber to adjust the temperature. A dimmer stat was used as a fixed voltage source to protect the variations in the operating temperature. A Keithley 6514 programmable computer connected electrometer was employed to record change in the sensor resistance with respect to time after inserting target gases in the stainless-steel chamber. For sensor measurements, thin films of $1.5 \times 1.5 \text{ cm}^2$ area were fixed and counted over the measurement unit (Scheme 2). The electrical contacts were drawn using commercial silver paste. The gas sensor response was calculated using following equation [16]:

$$S(\%) = \frac{R_a - R_g}{R_a} \times 100$$ (1)
where, $R_p$ is stabilized resistance of atmospheric air, $R_g$ is stabilized resistance of target gas. A static liquid–gas distribution analysis method was preferred for calculating the concentration of VOCs by applying the following formula [8]:

$$C(\text{ppm}) = \frac{22.4\rho T V}{273 MV} \times 1000$$

(2)

where, $C$ (ppm) is the concentration of target gases; $\rho$ is (g ml$^{-1}$) is the liquid density; $V$ is the volume of liquid ammonia ($\mu$L); $T$ is temperature (K), $M$ is the molecular weight of ammonia (g mol$^{-1}$), and $V$ is the stainless-steel chamber volume (L). In this study, the $M$, $\rho$ and $V$ for ammonia are constant for gas sensor measurement and are 17.03 g mol$^{-1}$, 0.68 g cm$^{-3}$, and 0.250L, respectively.

3. Results and discussion

3.1. Reaction mechanism

In hydrothermal synthesis a white-colored precipitate was settled at the bottom of the Teflon-lined autoclave. The plausible chemical reactions responsible for forming WO$_3$ NBs powder are proposed as equations (3)–(7) [17, 18]. The (NH$_4$)$_2$H$_2$W$_{12}$O$_{42}$.4H$_2$O was dissolved in H$_2$O. After an addition of strong HCl to this solution, the ammonium paratungstate can lose bonding stability by producing separate ions with a transparent solution (equation (3)). After the addition of H$_2$O$_2$, aqueous solution containing OH$^-$ ions under constant stirring, WO$_5^{2-}$ and H$^+$ react with OH$^-$ to produce WO$_3$.H$_2$O (equations (4)–(5)). As the reaction was kept under hydrothermal conditions, an intramolecular bonding process could be responsible for the conversion of WO$_3$.H$_2$O to WO$_3$.2(OH)$_2$ (equation (6)). Finally, the as-obtained white-colored WO$_3$(OH)$_2$ powder was air-calcinated for 1 h at 500 °C to form pale green WO$_3$ NBs (equation (7)).

$$(\text{NH}_4)_2[\text{H}_2\text{W}_{12}\text{O}_{42}].4\text{H}_2\text{O} + \text{HCl} + 2\text{H}_2\text{O} \leftrightarrow 10\text{NH}_4^+12\text{WO}_4^{2-} + 15\text{H}^+ + \text{Cl}^-$$

$$\text{H}_2\text{O}_2 \rightarrow 2\text{OH}^-$$

$$\text{WO}_4^{2-} + 4\text{H}^+ + 2\text{OH}^- \rightarrow \text{WO}_3\cdot\text{H}_2\text{O} + 2\text{H}_2\text{O}$$

$$\text{WO}_3\cdot\text{H}_2\text{O} \rightarrow \text{WO}_3\cdot(\text{OH})_2$$

$$\text{WO}_3(\text{OH})_2 \xrightarrow{500\ ^\circ\text{C}, 1\ h} \text{WO}_3$$

(3) (4) (5) (6) (7)

3.2. Optical transparency and surface morphology analyses

A representative FE-SEM image of the WO$_3$ product has demonstrated uniformly distributed surface morphology of NB arrays. The side-view (figure 1(a)) clearly shows that the surfaces of the WO$_3$ NBs were smooth with the approximately 100 nm of diameter and the 0.5 μm of length. Figure S1(a†), available online at stacks.iop.org/MRX/7/015076/mmedia demonstrates the low magnification FE-SEM image of WO$_3$ NBs. Figure S1(b†) shows the energy dispersive spectroscopy spectra of WO$_3$ NBs and the analyzed peaks confirmed the phase purity and the presence of W and O atoms. The carbon peaks present in the energy dispersive spectroscopy spectra are due to carbon tape used during FE-SEM scanning. Furthermore, the HR-TEM image of the as-prepared WO$_3$ NBs has approved a single crystalline character with fine and regular lattice fringes over scanned area (figure 1(b)). The 0.36 nm lattice spacing measured from the HR-TEM image, is closely supporting to (200) diffraction peak of monoclinic WO$_3$ [19]. The SAED pattern exhibited a regular sharp spot which is in accord with highly crystalline nature of the as-obtained WO$_3$ NBs. Notably, XRD spectrum evidenced the formation of polycrystalline WO$_3$ (discussed in the followed section), a little contradictory to SAED analysis, could be attributed to difference in the scanning areas of two measurements. The HR-TEM attached EDAX analysis highlights both W and O elements which are equivalently distributed throughout the product. The Cu peaks were also appeared due to the copper grade substrate used while scanning (figure 1(c)). Figure S2(a†) shows the optical absorbance spectrum at around 460 nm, evidencing a visible light transparency signature. The inset of figure S2(a†) presents the Tauc plot for WO$_3$ film (1.5 μm thickness estimated from cross-sectional image), from which the $E_g$ was estimated. The 2.82 eV $E_g$ value for the WO$_3$ NBs film is closely matching to a number results reported previously [20]. The DTA measurement (figure S2(b†)) was used to confirm the thermal behavior of the material. The DTA measurement depicted two peak positions, relatively small endothermic peak at 36.4 °C and broad exothermic peak at 221.3 °C for the removal of water molecule and the synthesized WO$_3$ phase from WO$_3$.H$_2$O [21].

3.3. Structural elucidation

The XRD pattern was used to confirm phase purity and crystal plane of the WO$_3$ NBs. As-seen in figure 2(a), the XRD plane revealed the diffraction peaks of monoclinic crystal phase with $a = 0.7297$ nm, $b = 0.7539$ nm, $c = 0.7688$ nm and $\beta = 90.91^\circ$ which is in close agreement with known data (ICPDS card no. 43-1035).
Presence of broad and strong diffraction peaks is approving polycrystalline signature of the as-obtained WO₃ NBs film. A strongly preferential growth direction [200] is noticed. In figure 2(b), the sharp Raman bands were found at 805 and 718 cm⁻¹ (O–W–O stretching vibration modes). The Raman bands noted at 271 and 310 cm⁻¹ (O–W–O bending vibration modes of the bridging oxygen) were the characteristics of monoclinic WO₃. The wavenumber 672 cm⁻¹ demonstrated stretching and bending vibrations of the connecting tungsten and oxygen atoms [22]. The XPS spectroscopy measurement provides a valuable quantitative and chemical state information of the material. Two 4f⁷/₂ (35.7 eV) and 4f⁵/₂ (37.6 eV) peaks, due to a dual state of tungsten, were corroborated in a wide XPS scan (figure 3(a)). In consistent to literature value, the W4f core-level at 35.3 eV was 37.8 eV. The W4f spectrum with metal and oxide presents the 4f⁷/₂-4f⁵/₂ doubles match to the W⁶⁺ oxidation state from WO₃ [23]. The XPS as depicted in figure 3(b) suggested the origin of oxygen vacancies as main peak is O₁s. The two O₁s, peaks confirmed binding energies at 530.3 and 531.7 eV for WO₃ NBs structure. The peak at 530.3 eV might be due to oxygen lattice and O²⁻ ions, and peak at 531.7 eV could be related to the ions of O²⁻, O⁻, and OH⁻ in the region of oxygen-deficiency [24].

3.4. Surface area and pore-size distribution studies
To determine the specific surface area, and pore-size distribution of the WO₃ NBs, the nitrogen adsorption-desorption isotherm was measured and is shown in figure 4. The nitrogen adsorption-desorption isotherm
demonstrated type IV hysteresis loop at relative pressure \( P/P_0 \) between 0.4 and 1.0, suggesting the presence of mesoporous nature \([25]\). According to the BET method, a typical value for the specific surface area was 38.74 m\(^2\)g\(^{-1}\). The inset plot of the as-obtained WO\(_3\) NBs exhibited a small pore-size distribution centered at 10.76 nm. The average specific surface area and small pore-size distribution of WO\(_3\) NBs would facilitate easy mass/charge transportation for gas molecules with a high sensitivity (discussed below) \([26]\).

3.5. Gas sensing properties
Sensitivity and selectivity are two significant parameters for gas sensor measurement. From a commercial point of view, the sensors must possess a good selectivity and high sensitivity, as well as considerable stability. In this study, we measured the sensitivities of the WO\(_3\) NBs film as a sensor material toward five VOCs at a fixed 100 ppm concentration, namely: ammonia, acetone, methanol, ethanol, and toluene. Figure 5(a) shows the gross sensitivity measurements towards VOCs, where the WO\(_3\) NBs sensor demonstrated higher sensitivity at room temperature for ammonia (figure 5(a)). The WO\(_3\) sensor was almost insensitive for methanol and toluene. In figure 5(b), the impact of various temperatures on the gas sensor performance for 100 ppm ammonia was evaluated. The WO\(_3\) NBs sensor produced a maximum response of 75% for 100 ppm ammonia at room-temperature. This can be elucidated with the help of following reasons. Firstly, the mesoporous structures could favor a higher surface area of WO\(_3\) NBs that can facilitate easy adsorption of excessive gas molecules. The amount of O\(_2\) species present at material surface can be enhanced by increasing the surface area and pore engineering, which can provide more active sites for adsorption of gas molecules \([27]\). Secondly, the higher
temperatures might suppress the gas adsorption by rising the operation rate. Finally, as ammonia is unstable at higher temperatures, lower response values can be resulted [2]. Figure 5(c) demonstrates the dynamic response of WO3 NBs sensors ranging from 10 to 1000 ppm levels of ammonia concentrations. The gas response enhanced with ammonia concentration and was sensitive even at less than 10 ppm of ammonia. In sensor measurement, the response transient curve showed that the resistance reached almost to its original value after the exclusion of ammonia gas, indicating excellent gas sensor reversibility [28]. The responses of the sensor upon exposure to 10, 50, 100, 200, 400, 800 and 1000 ppm of ammonia concentrations were respectively 35, 52, 75, 88, 108, 127 and 132%. The low response at 10 ppm ammonia concentration was due to lower adsorption of ammonia molecules, thereby there could a slow sensing reaction rate. The higher response at 1000 ppm ammonia concentration was because of a larger quantity of ammonia gas molecules adsorbed on the reaction surface. However, there was no significant increase in the response for 800 and 1000 ppm concentrations of ammonia, which might be because of the limited accessibility of active surface sites on the sensing material surface for adsorption reaction. Furthermore, figure 6(a) demonstrates the transient resistance versus time curve of WO3 NBs sensors with 100 ppm of ammonia. Notably, on exposing the reducing ammonia, the resistance of the sensor material drastically decreased (for 8 s), then stabilized after some time. The gas sensor recovery was measured by exposing atmospheric air in sensing chamber, confirmed an excellent recovery in just 5 s. The 8/5 s response/recovery time of the WO3 NBs film sensor represented its ultrafast sensing activity for potential commercial viability. The response/recovery time of gas sensors mainly depends on how quick the gas diffuses in/out [29]. The response/recovery time is an imperative parameter for calculating the gas-sensing performance of a material. Ideally, both should be equal. But, the presence of stacking faults, active sites and structural irregularities make them different. The response/recovery time achieves a maximum sensing response of 90% on exposure to target gases/time and decreases to 10% upon air exposure [30]. The fast response/recovery time of the WO3 NBs film sensor was because of its special NB-typemorphology, allowing an easy and fast adsorption/desorption of ammonia gas molecules, which is one of the appealing measurements. Figure 6(b) shows transient response and recovery curves for 100 ppm of ammonia concentration at room temperatures.
temperature. From the gas response curve, the WO₃ NBs sensor demonstrate a highest response of 75% at 100 ppm concentration of ammonia gas within 8 s response time which is better than 92% at 250 ppm (4 min response time) reported by Mintcheva et al for Sn-Zn alloy–based room-temperature sensors [31]. The quick response/recovery time could be due to the higher surface area (38.74 m²g⁻¹); this increased surface area is responsible for higher adsorption of the target gas because one-dimensional morphology promotes a faster charge transportation. The higher surface area and NB-type surface morphology of WO₃ could have assisted a better room-temperature gas sensing performance. A reproducibility test of the WO₃ NBs sensor at 100 ppm of ammonia was also studied and is revealed in figure 6(c). The sensor response remained nearly same during continuous-cycling stability tests. Gas sensor devices should avail not only a high sensitivity for the target gases, but also a better stability [32]. Figure 6(d) shows the cyclic stability test of WO₃ NBs sensor film measured at a concentration of 100 ppm ammonia for the period of 15 days time. The response remained closed to 75% at 100 ppm concentration of ammonia gas, suggesting industrial potential of WO₃ NB-based gas sensors.

3.6. Sensing mechanism

The gas sensing mechanism is shown in schematic diagram (scheme 3). The (metal oxide-based) gas sensing mechanism can be elucidated through changing depletion layer of oxygen adsorption. The WO₃ is n-type semiconductor material, and therefore electrons are the essential source of charge carriers [33]. When WO₃ sensor film is open to ambient air, the air molecules of oxygen adsorb on its surface by withdrawing electrons to form surface adsorbed oxygen species, which eventually can reduce the number of electrons from the conduction band of WO₃. The oxygen adsorbed on surface of the WO₃ sensor film helps to manipulate the resistance of the gas sensor as the adsorbed oxygen is temperature dependent [34]. In our case, O₂ is dominant as the WO₃ sensor is operated at room temperature. Before exposure to ammonia, care should be taken that the resistance of the WO₃ NBs sensor should be stabilized. It can be seen that, in presence of ammonia, resistance of WO₃ NBs sensor decreased quickly with respect to time, and stable resistance was accomplished within few seconds (8 s), suggesting a rapid response to ammonia. Upon the interface of ammonia with the WO₃ NBs sensor, the previously adsorbed O₂ species could play a major role in the reaction. Consequently, adsorbed oxygen species get replaced with ammonia molecules because of their reducing character, decreasing the resistance of the WO₃ NBs sensor. A plausible ammonia sensing mechanism
through chemical reactions can be as follows [35]:

$$\text{O}_2^{\text{air}} \rightarrow \text{O}_2^{\text{ads}}$$  \hspace{1cm} (8)

$$\text{O}_2^{\text{ads}} + e^- \rightarrow \text{O}_2^{\text{ads}}$$  \hspace{1cm} (9)

$$\text{NH}_3^{\text{g}} + 5\text{O}_2^{\text{ads}} \rightarrow 4\text{NO} + 6\text{H}_2\text{O} + 5e^-$$  \hspace{1cm} (10)

Further, the gas sensing reaction mechanism might be elucidated with the following points. Firstly, WO$_3$, being a metal oxide, follows an electron transport mechanism similar to other metal oxides. The electron transportation takes place from WO$_3$ to O$_2$, and potential barrier is taking place at the surface of sensor material. The resulting potential barrier hinders electron transportation throughout the material; subsequently, the sensing layer surface adsorbs a large number of oxygen species, which can enhance the gas sensor performance. Secondly, the capability of test molecules to arrive on the depletion region also determines the sensing performance of materials [36]. This is a well-known phenomenon: if the size of the gas molecule is smaller there is more probability of penetrating through the depletion region. The ammonia molecule has the lowest (kinetic diameter of 0.26 nm [37]) compared with ethanol (0.45 nm) and acetone (0.469 nm) molecules [38]. Therefore, the gas sensitivity towards ammonia is higher compared to the other VOCs that we considered. Thirdly, particle size can also be acknowledged as a parameter for gas sensing behavior. In the case of WO$_3$, the Debye length is approximately 33 nm [39], which is much smaller than the size (i.e., 85 nm) of WO$_3$ NBs. Therefore, the gas sensing mechanism of WO$_3$ NBs follows the Schottky-barrier-controlled model. Moreover, porosity also plays an important role in the gas sensing behavior of sensor materials. The calculated average pore-size was in the range of 10–15 nm, suggesting a mesoporous nature of the materials [40].

### 3.7. Humidity sensing activity

The humidity-sensing performance of WO$_3$ NBs film sensor was carried out using a binary electrode under various (20–80%) relative humidity (RH) conditions. Saturated salt solutions were used to monitor RH conditions at room-temperature and variations in the resistance of WO$_3$ NBs film sensor under 20% RH conditions are shown in figure 7(a). The saturated salt solution contains H$_2$O molecules that can act as electron donors, and thereby, the film resistance of WO$_3$ NBs sensors dropped down with the RH conditions. The humidity-sensing mechanism, the Fermi level, of a material which is nearby to the conduction band edge could modify after adsorbing H$_2$O molecules on the surface of the sensor [41]. The response/recovery time of the WO$_3$ NBs sensor was 10.8 s. The ultra-fast response (10 s)/recovery time (8 s) was determined by the NBs type of WO$_3$ architecture and the fast desorption process of H$_2$O molecules from the WO$_3$ NBs sensor surface, respectively; resulting in the fast adsorption/desorption of H$_2$O molecules. Bharatula et al reported that the thermodynamic adsorption of analyte molecules may not be favorable due to strong adsorption/desorption at room temperature. During this process, the analyte molecules get desorbed easily due to the low adsorption energy, which leads to an increase in the response time compared to the recovery time [42]. The result of various RH conditions on sensor sensitivity is shown in figure 7(b); thus, confirming an improvement in the response of the WO$_3$ NBs sensor to humidity with the RH conditions. It was concluded that, in addition to ammonia, hydrothermally-synthesized WO$_3$ NBs sensors directed an ultra-high response/recovery time for humidity as well. The room-temperature sensitivities of 75 and 33% were obtained for the WO$_3$ NBs sensor for ammonia and humidity, respectively; suggesting its practical and commercial perspectives. The gas sensing performance...
of WO₃ NBs sensor was correlated with previously reported data (shown in table 1), wherein higher response values for ammonia sensing were noticed. In previous studies, the sensor operating temperature was a major constraint; plus, doping of noble metals and metal oxides into the host WO₃ materials were introduced to enhance the sensor response. Present WO₃ NBs film sensors detect ammonia with considerable response at room temperature, which has its own credentials.

4. Conclusions

In conclusion, mesoporous WO₃ NBs were prepared via a simple and cost-effective hydrothermal synthesis method. A film of WO₃ NBs was fabricated directly onto a borosil-glass substrate using a doctor-blade method. The gas sensing performance of WO₃ NBs sensor was measured for the detection of ammonia and humidity at room-temperature (27 °C). The highest response of 75% and ultrafast 8 s response/recovery time were obtained at 100 ppm concentration of ammonia. In addition, an excellent humidity response (32%) was displayed by the WO₃ NBs sensor at a relative humidity (RH) of 20%. The fast response time (10 s) of humidity sensing is due to the hydrophilic surface of the WO₃ NBs can be accounted for a slow H₂O molecules adsorption and an ultra-fast recovery time of 8 s; this could be because of the rapid desorption of H₂O molecules on the surface of WO₃ NBs.

Acknowledgments

The authors would like to extend their sincere appreciation to the Researchers supporting project number (RSP-2019/55), King Saud University, Riyadh, Saudi Arabia.
References

[1] Kwak D, Lei Y and Maric R 2019 Ammonia gas sensors: a comprehensive review Talanta 204 713–30
[2] Ghule B G, Shaikh S, Ekar S U, Nakate U T, Gunturk K C, Shinde N M, Naushad M, Kim K H, O’Dwyer C and Mane R S 2017 Natural carbonized sugar as a low-temperature ammonia sensor material: experimental, theoretical, and computational studies ACS Appl. Mater. Interfaces 9 43051–60
[3] Gu F, Cui Y, Han D, Hong S, Flytzani-Stephanopoulos M and Wang Z 2019 Atomically dispersed Pt (II) on WO3 for highly selective sensing and catalytic oxidation of triethylamine Appl. Catal. B Environ. 256 117809
[4] Wu C-H, Zhu Z, Huang S-Y and Wu R-J 2019 Preparation of palladium-doped mesoporous WO3 for hydrogen gas sensors J. Alloys Compd. 776 963–73
[5] Wang Z, Chiu H-C, Paolella A, Zaghb K and Demopoulos G P 2019 Lithium Photo-intercalation of CdS-Sensitized WO3 anode for energy storage and photoelectrochemical applications Chem. Soc. Rev. 122 2220–30
[6] Zhang J, Lu H, Yan C, Yang Z, Zhu G, Gao J, Yin F and Wang C 2018 Fabrication of conductive graphene oxide–WO3 composite nanofibers by electrospinning and their enhanced acetone gas sensing properties Sensors Actuators B Chem. 264 128–38
[7] Wang C, Sun R, Li X, Sun Y, Sun P, Liu F and Lu G 2014 Hierarchical flower-like WO3 nanostructures and their gas sensing properties Sensors Actuators B Chem. 204 234–39
[8] Ahmed I, Ahmad T, Ubaidullah M, Al-Enizi A M, Alhabarah A N, Alshehri N and Alshehri S M 2019 rGO supported NiWO4 nanocomposites for hydrogen evolution reactions Mater. Lett. 240 51–4
[9] Shaikh S F, Mane R S, Min B K, Hwang Y J and Joo O-S 2013 Monoclinic WO3 nanorods Sensors Actuators B Chem. 193 3–14
[10] Siciliano T, Tepore A, Micocci G, Serra A, Manno D and Filippo E 2008 WO3 gas sensors prepared by thermal oxidation of tungsten Sensors Actuators B Chem. 133 321–6
[11] Caiteanu D, György E, Grigorescu S, Mihaiescu I N, Prodan G and Ciupina V 2006 Growth of oxide thin films of tungsten solid-state operation Solid. State. Electron. 47 827–30
[12] Teoh L G, Hon Y M, Shieh J, Lai W H and Hon M H 2003 Sensitivity properties of a novel NO2 gas sensor based on mesoporous WO3 thin film sensors Sensors Actuators B Chem. 96 219–23
[13] Kim Y S et al 2005 Room-temperature semiconducting gas sensor based on nonstoichiometric tungsten oxide nanorod film Appl. Phys. Lett. 86 213105
[14] Zheng F, Song S, Lu F, Li R, Bu N, Liu J, Li Y, Hu P and Zhen Q 2016 Hydrothermal preparation of graphene oxide/WO3 nanofiber films Sensors Actuators B Chem. 226 4582–6
[15] Martin A J, Maffiotta C and Chaparro A M 2015 Mechanisms for the growth of thin films of WO3 and bronzes from suspensions of WO3 nanoparticles ECS Trans. 64 43–56
[16] Mahmood K, Swain B S, Kirimani A R and Amassian A 2015 Highly efficient perovskite solar cells based on a nanostructured WO3–TiO2 core–shell electron transporting material J. Mater. Chem. A 3 9051–7
[17] Shaikh S F, Kalanur S S, Mane R S and Joo O-S 2015 Monoclinic WO3 nanorod–rutil TiO2 nanoparticles core–shell interface for efficient DSSCs Dalt Trans. 42 10085–8
[18] Chen D, Gao L, Yasumori A, Kuroda K and Sugahara Y 2008 Size- and shape-controlled conversion of tungstate-based inorganic–organic hybrid belts to WO3 nanoplates with high specific surface areas Small 4 1813–22
[19] Kalanur S S, Yoo I-H, Cho I-S and Seo H 2019 Effect of oxygen vacancies on the band edge properties of WO3 producing enhanced photocurrents Electrochim. Acta 296 517–27
[20] Kanwat A and Jang J 2014 Extremely stable organic photovoltaic incorporated with WO3 doped PEDOT:PSS anode buffer layer J. Mater. Chem. C 2 3901–7
[21] Wang T, Quan W, Jiang D, Linlin C, Li D, Meng S and Chen M 2016 Synthesis of redox–mediator-free direct Z-scheme AgI/WO3 nanocomposite photocatalysts for the degradation of tetracycline with enhanced photocatalytic activity Chem. Eng. J. 300 280–290
[22] Li J, Liu X, Han Q, Yao X and Wang X 2013 Formation of WO3 nanotube-based membranes directed by NaHSO4 and its application in water treatment J. Mater. Chem. A 1 1246–53
[23] Tian S, Ding X, Zeng D, Zhang S and Xie C 2013 Pore-size–dependent sensing property of hierarchical SnO2 mesoporous microfibers as formaldehyde sensors Sensors Actuators B Chem. 186 640–7
[24] Li Y, Zhan W, He Y, Wang Y, Kong X, Kuang Q, Xie Z and Zheng L 2014 MOF-templated synthesis of porous Co3O4 concave nanocubes with high specific surface area and their gas sensing properties ACS Appl. Mater. Interfaces 6 4186–95
[25] Cui S, Pu H, Lu G, Wen Z, Mattson E C, Hirschmugl C, Gajdardziska-Josifovska M, Weinfert M and Chen J 2012 Fast and selective room-temperature ammonia sensors using silver nanocrystal-functionalized carbon nanotubes ACS Appl. Mater. Interfaces 4 4898
[26] Navale S T, Jadhav V V, Tehare K K, Sagar R U R, Bivasw C S, Galluzzi L, Liang W, Patil V B, Mane R S and Stadler F J 2017 Solid-state synthesis strategy of ZnO nanoparticles for the rapid detection of hazardous Cl2 Sens. Actuators B Chem. 238 1102
[30] Pawbake A S, Waykar R G, Late D J and Jadhark R S 2016 Highly transparent wafer-scale synthesis of crystalline WS2 nanoparticle thin film for photodetector and humidity-sensing applications ACS Appl. Mater. Interfaces 8 3359
[31] Mintcheva N, Aljulaih A A, Bito S, Honda M, Kondo T, Iwamori S and Kulminich S A 2018 Nanomaterials produced by laser beam ablating Sn-Zn alloy in water J. Alloys Compd. 747 166–75
[32] Tang Y, Tehan E C, Tao Z and Bright F V 2003 Sol–gel-derived sensor materials that yield linear calibration plots, high sensitivity, and long-term stability Anal. Chem. 75 2407–13
[33] Su J, Guo L, Bao N and Grimes C A 2011 Nanostructured WO3/BiVO4 heterojunction films for efficient photoelectrochemical water splitting Nano Lett. 11 1928–33
[34] Shinde P V, Xia Q X, Ghule B G, Shinde N M, Seonghee J, Kim K H and Mane R S 2018 Hydrothermally grown α-MoO3 interlocked mesoporous micro-cubes of several nanocrystals as selective and sensitive nitrogen dioxide chemoresistive gas sensors Appl. Surf. Sci. 442 178–84
[35] Zhang D, Jiang C, Li P and Sun Y E 2017 Layer-by-layer self-assembly of Co3O4 nanorod-decorated MoS2 nanosheet-based nanocomposite toward high-performance ammonia detection ACS Appl. Mater. Interfaces 9 6462
[36] Rakshit S, Santra S, Mann A I and Ray S K 2014 Enhanced sensitivity and selectivity of brush-like SnO2 nanowire/ZnO nanorod heterostructure based sensors for volatile organic compounds RSC Adv. 4 36749–56
[37] Kanezashi M, Yamamoto A, Yoshioka T and Tsuru T 2010 Characteristics of ammonia permeation through porous silica membranes AIChE J. 56 1204–12
[38] Du X and George S M 2008 Thickness dependence of sensor response for CO gas sensing by tin oxide films grown using atomic layer deposition Sensors Actuators B Chem. 135 152–60
[39] Tamaki J, Zhang Z, Fujimori K, Akiyama M, Harada T, Miura N and Yamazoe N 1994 Grain-size effects in tungsten oxide-based sensor for nitrogen oxides J. Electrochem. Soc. 141 2207–10
[40] Meng F, Ge S, Jia Y, Sun B, Sun Y, Wang C, Wu H, Jin Z and Li M 2015 Interlaced nanoflake-assembled flower-like hierarchical ZnO microspheres prepared by bisolvents and their sensing properties to ethanol J. Alloys Compd. 632 645–50
[41] Xie G, Yu J, Chen X and Jiang Y 2007 Gas sensing characteristics of WO3 vacuum deposited thin films Sensors Actuators B Chem. 123 909–14
[42] Bhalatula L D, Erande M B, Mulla I S, Rout C S and Late D J 2016 SnS2 nanoflakes for efficient humidity and alcohol sensing at room temperature RSC Adv. 6 105421–7
[43] Qiang X, Hu M, Zhao B, Qin Y, Zhang T, Zhou L and Liang J 2018 Preparation of porous silicon/Pd-loaded WO3 nanowires for enhancement of ammonia sensing properties at room temperature Mater. Sci. Semicond. Process. 79 113–8
[44] Wang Y et al 2017 NH3 gas sensing performance enhanced by Pt-loaded on mesoporous WO3 Sensors Actuators B Chem. 238 473–81
[45] D’Arienzo M, Amelio L, Mari C M, Polizzi S, Ruffo R, Scirti R and Morazza Z 2011 Macroporous WO3 thin films active in NH3 sensing: role of the hosted Cr isolated centers and Pt nanoclusters J. Am. Chem. Soc. 133 3296–304
[46] Srivastava V and Jain K 2008 Highly sensitive NH3 sensor using Pt catalyzed silica coating over WO3 thick films Sensors Actuators B Chem. 133 46–52
[47] Llobet E, Molas G, Molina S, Calderer J, Vilanova X, Brezmes J, Sueiras J E and Correig X 2000 Fabrication of highly selective tungsten oxide ammonia sensors J. Electrochem. Soc. 147 776–9
[48] Balazsi C, Wang L, Zayim E O, Szilágyi I M, Sedlacková K, Pfeifer J, Tóth A L and Gouma P-I 2008 Nanosize hexagonal tungsten oxide for gas sensing applications J. Eur. Ceram. Soc. 28 915–7
[49] Stankova M, Vilanova X, Llobet E, Calderer J, Bittencourt C, Pireaux J J and Correig X 2005 Influence of the annealing and operating temperatures on the gas-sensing properties of r-f sputtered WO3 thin-film sensors Sensors Actuators B Chem. 105 271–7