Enhanced ethanol sensing properties of WO$_3$ modified TiO$_2$ nanorods

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Abstract: Pristine and WO$_3$ decorated TiO$_2$ nanorods (NRs) were synthesised to investigate n-n-type heterojunction gas sensing properties. TiO$_2$ NRs were fabricated via hydrothermal method on fluorine-doped tin oxide coated glass (FTO) substrates. Then, tungsten was sputtered on the TiO$_2$ NRs and thermally oxidised to obtain WO$_3$ nanoparticles. The heterostructure was characterised by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) spectroscopy. Fabricated sensor devices were exposed to VOCs such as toluene, xylene, acetone and ethanol, and humidity at different operation temperatures. Experimental results demonstrated that the heterostructure has better sensor response toward ethanol at 200 °C. Enhanced sensing properties are attributed to the heterojunction formation by decorating TiO$_2$ NRs with WO$_3$.

Key words: WO$_3$/TiO$_2$, gas sensor, heterostructure, nanorods, ethanol

1. Introduction

Volatile organic compounds (VOCs) such as ethanol, acetone, toluene, xylene have been widely used in daily life, especially in industrial applications. However, VOCs induce some harmful effects for human health and environment [1-6]. In addition, some VOCs have been referred as tracer compounds in the human exhaled breath for various diseases [7-9]. Moreover, ethanol is the strongest indicator for detection of alcohol level in human breath [10]. Therefore, proper and fast detection of various VOCs is very important for different applications such as, traffic security, environmental monitoring, in-door air quality and breath analysis.

There are many detection techniques for VOCs such as optical, spectroscopic, chromatographic, electrochemical [11-13]. Among all these techniques, semiconductor metal oxide (SMO) based chemi-resistive gas sensors are one of the best candidates due to their high sensitivity and easy production processes [14-16]. Moreover, different techniques such as loading with a catalyst, doping a host element, or heterostructural fabrication of SMO materials may improve their gas sensing properties against various gas species [17-22]. Therefore, SMOs are superior sensing materials for VOCs detection.

As an n-type semiconductor, TiO$_2$ is one of the most used material for VOCs detection for many years. TiO$_2$ has some distinctive features such as its nontoxic nature, easy nanostructural fabrication, and superior reaction ability to a wide range of VOCs. Especially, one dimensional (1D) TiO$_2$ nanomaterials such as nanorods and nanotubes have been widely used due to their higher surface-to-volume ratio [23-27]. However, some sensor properties such as selectivity and operation temperature must be still improved for specific applications. Therefore, scientists are interested in heterostructured metal oxides such as TiO$_2$, to increase their sensing performances. The sensing performances of heterojunction enhance in virtue of band alteration at the interface between different materials. This provides charge transfer through the interface from one material to another by creating charge-space region and adsorption sites [17, 28-32]. WO$_3$ is one of the best candidates for heterostructure due to its highly reactive nature against various VOCs [33,34]. WO$_3$/TiO$_2$ heterostructures have been widely investigated for photocatalytic, thermochromic and supercapacitor applications [35-37]. However, investigation of gas sensing properties of WO$_3$/TiO$_2$ heterostructures is still limited. L.E. Depero et al. [38] and D-S. Lee et al. [39] fabricated TiO$_2$-WO$_3$ sensors with sputtering and co precipitation methods, respectively, and explored their NO$_x$ sensing performances. Y. Yao et al. [40] fabricated TiO$_2$-WO$_3$ composite coatings and explained the enhanced methane sensing properties by creation of heterojunctions between the TiO$_2$ and WO$_3$ interface. S.M. Zanetti et al. investigated the WO$_3$ doping effect on TiO$_2$ nanocrystalline powders and estimated their excellent humidity sensing properties [41]. W. Meng et al. synthesised TiO$_2$ powder-core WO$_3$ shell composite sensing electrode and demonstrated

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a better NH$_3$ sensing performance [42]. Even though, MOX heterostructures have potential applications in chemical gas sensors [43-45], there are limited study on the sensing properties of WO$_3$/TiO$_2$ NRs heterostructures. Especially, studies with various WO$_3$ loading are considerably poor.

In this study, WO$_3$/TiO$_2$ NRs with various WO$_3$ loading were obtained for chemical gas sensors. The enhancing sensor performance of SMO gas sensors with decorating of highly ordered 1D n-type TiO$_2$ NRs by n-type WO$_3$ is the motivation of this study. Highly ordered TiO$_2$ NRs were synthesised by hydrothermal method on TiO$_2$ seed-layer coated FTO substrates. Then, WO$_3$ layers were coated on TiO$_2$ NRs by magnetron sputtering technique with different thicknesses. Structural and morphological characterisation of WO$_3$/TiO$_2$ heterostructures were investigated. Gas sensor performances of heterostructures were studied against ethanol, toluene, xylene, acetone and humidity at various temperatures.

2. Materials and methods

FTO substrates (8 Ω/sq) was obtained from Sigma-Aldrich (ChemieGmbH, Hamburg, Germany). Hydrochloric acid (HCl, 37%) was acquired from Sigma-Aldrich. Titanium (IV) isopropoxide (TTIP, 97 +%) and sodium tungsten oxide dihydrate (Na$_2$WO$_4$·2H$_2$O, 95%, crystalline) were provided from Alfa Aesar (city, country?). Titanium target (Ti, 99.995% purity and 2.00" diameter × 1.25" thick) and tungsten target (W, 99.95% purity and 2.00" diameter × 1.25" thick) were purchased from Kurt J. Lesker Company (city, country?). Distilled (DI) water (18 MΩ) was utilised through the all experiments.

2.1. Fabrication of WO$_3$ modified TiO$_2$ NRs heterostructures

The WO$_3$/TiO$_2$ heterostructures were obtained on the basis of different studies in the literature. A compact TiO$_2$ seed-layer with a thickness of approximately 50 nm was deposited on the FTO substrate to prevent shorting before the growth of TiO$_2$ NRs as reported previously in literature [46]. First, FTO substrates were purified by acetone, isopropanol and DI water in ultrasonic bath for 10 min, respectively. Then, Ti seed-layer was deposited by RF magnetron sputtering on the FTO substrates. Sputtering of Ti thin film (TF) process was performed in 5m Torr Ar atmosphere, with applied power of 100 W for 25 min. Finally, samples were annealed in the air atmosphere at 500 °C for 3 h. During the thermal oxidation process, Ti layer reacts with oxygen molecules in the air and transforms to TiO$_2$ layer [47].

TiO$_2$ NRs were synthesised by hydrothermal method on TiO$_2$ seed-layer coated FTO substrates. Firstly, 40 mL DI water and 40 ml HCl was mixed. Then, 0.9 ml TTIP was added drop by drop on previously mixed solution. Finally, the resulting mixture was stirred for 1 h at room temperature to obtain a homogeneous solution. This precursor solution was poured into a 250 mL autoclave, and TiO$_2$ seed-layer coated FTO substrates were placed vertically into the autoclave. Then the autoclave was sealed, placed into the temperature-controlled oven and thermally treated at 170 °C for 15 h [22, 48]. After thermal treatment, the samples were removed from autoclave, rinsed in DI water and dried under dry air flow.

WO$_3$ layer was deposited on TiO$_2$ NRs by the thermal oxidation method. Firstly, W layer was deposited by RF magnetron sputtering. Deposition of W layer was performed at 5 m Torr with RF power of 120 W for 1, 2, and 3 min under Ar atmosphere. Then, deposited W layer was thermally oxidised at 450 °C for 1 h to obtain the WO$_3$ layer [49]. Sensor fabrication process was illustrated in Figure 1. Pristine TiO$_2$ NRs sample was named as TiO$_2$, and WO$_3$-modified TiO$_2$ NRs samples were named as WT-1, WT-2 and WT-3 in accordance with W deposition time of 1, 2, and 3 min, respectively.

![Figure 1. Schematic illustration of WO$_3$/TiO$_2$ NRs fabrication process.](image-url)
The morphological and structural characterisations of fabricated samples were performed by scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDX) (Philips XL 30S) and X-ray diffraction (XRD) (Rigaku D-max, RINT-2200 series, X-ray diffractometer with Cu-Kα radiation, λ = 0.15418 nm), respectively.

2.2. Gas sensing measurements

WO₃-decorated TiO₂ NRs were examined for VOCs and humidity sensing performance. To perform electrical measurements, aluminium contact electrodes (thickness 200 nm) were evaporated on the samples with Leybold Univex 450 (city, country?) thermal evaporation system. Schematic illustration of sensor fabrication was given in Figures 2a and 2b. The sensors were placed into a test chamber with 1 L in volume. A high purity dry air was connected to the test chamber. The dry air flow and the concentration of gases were controlled by flow meters and a multi gas controller – MKS 647C. Working temperature of devices was controlled by a Lakeshore 340 (city, country?). Keithley 6517A electrometer (city, country?) was used for current vs. time characteristics during gas sensing measurements. The atmosphere in the test chamber was cleaned by dry air flow. When the electric current reached a steady value, VOCs was sent to the test chamber. Humidity sensing performances of the sensors were also characterised. VOCs were generated by bubbling method [25]. Antoine’s equation was used to calculate VOCs’ concentration. All data were reported as a sensor response defined as follows [50];

$$S_R = \frac{\Delta I}{I_0},$$

where \(\Delta I\) is the change in the current value when sensors were exposed to target gas molecules, \(I_0\) is the baseline current value measured under dry air flow condition. Response (t₉₀ res) and recovery (t₉₀ rec) times are defined as the time required the sensor to achieve 90% \(\Delta I\) of its current form [51,52].

3. Results and discussion

3.1. Material characterisation

The surface morphology and elemental analysis were performed by SEM and EDX, respectively. The SEM images indicate that TiO₂ NRs are vertically aligned and homogenously covered on the substrate surface as seen in Figure 3a. The NRs were approximately 100 nm in diameter and 4.18 µm in length (Figure 3a inset). Figures 3b-3d show increasing amount of WO₃ layer on the TiO₂ NRs. The amount of WO₃ depends on W sputtering time. Figure 4 shows the presence of the titanium, tungsten and oxygen in the rods. EDX spectrum of the samples in Figure 4a shows that tungsten is not present in TiO₂ sample and atomic distribution of W are 0.5%, 0.94% and 1.11% in WT-1, WT-2 and WT-3 samples, respectively. The amount of W particles is correlated with sputtering time of W. The EDX mapping of WT-3 is given in Figure 4b. W particles homogeneously covered the surface of TiO₂ NRs as seen in Figure 4b.

XRD patterns of the samples are given in Figure 5. According to the XRD patterns, the diffraction peaks 36.1° and 62.8° were attributed to (101) and (002) crystal planes of rutile TiO₂, respectively (PDF card number 00-021-1276). The intensity of the diffraction peaks 36.1° and 62.8°, which refer to rutile TiO₂, decrease in samples WT-1, WT-2 and WT-3. This can be explained by decorating of TiO₂ NRs with WO₃ [53]. In addition, there are no observed diffraction peaks related with WO₃ in the XRD pattern, which might be due to poor signal formation from small amount of material loading. In order to identify the WO₃ XRD pattern, WO₃ TF with a thickness of 50 nm (WO₃-50) was deposited by RF magnetron sputter system, and subsequently thermal oxidised on FTO substrate. In Figure 6 comparative XRD results are shown for WO₃-50, WT-3 and pristine FTO substrate. Diffraction peaks at 2θ = 23.2°, 24.54°, 33.1° and 34° can be assigned to monoclinic WO₃ (002), (200), (022) and (220) reflections, respectively (PDF card number 00-043-1035). The peaks which marked as “S” belong to FTO substrate (PDF card number 00-046-1088).
Growth of TiO$_2$ NRs can be explained with two continuous reactions;

$$Ti(OR)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4ROH \quad \text{(hydrolysis)}$$

$$Ti(OH)_4 \rightarrow TiO_2, xH_2O + (2 - x)H_2O \quad \text{(condensation)}$$

where R is ethyl, i-propyl, n-butyl, etc. [54].

Firstly, hydrolysis occurs by reaction of TiO$_2$ precursor (TTIP) with water and TTIP transforms to titanium alkoxide. Then, titanium alkoxide forms a complex with water. The acidic platform controls the rate of complex formation. Finally, the high temperature and pressure condition accelerates hydrolysis process and appeared complex starts to deposit onto the substrate as TiO$_2$ NRs in rutile phase [55]. The fundamental reason of growing highly ordered NRs in the deposition process of titanium complexes onto the substrate is surface energy. In the TiO$_2$ phase, the lowest surface energy has (110) face. It means that [001] direction, parallel to (110) plane, is the theoretically preferable growth direction. The powerful (002) pick in XRD pattern is the proof of the growth of the highly aligned TiO$_2$ NRs along [001] direction [56].

3.2. Gas sensing properties

Gas sensor measurements of fabricated sensors were performed under toluene, xylene, acetone, ethanol, and relative humidity ambient in an operation temperature range between 100 °C and 250 °C. There was no observed sensor response signal from all the samples against any gases at 100 °C. Also, pristine TiO$_2$ and WO$_3$/TiO$_2$ heterostructures could not sense acetone molecules for all operation temperatures. Operation temperature dependent sensor response results of all sensors are given in Figure 7 with bar diagrams.

After all sensor measurements at different operation temperatures, 200 °C is identified as the optimal operation temperature for all sensors due to the highest sensor response values against each gas. At the optimal operation temperature,
WT-1 sensor showed an excellent sensing performance against 1850 ppm ethanol as seen in Figure 7b. Sensor performance toward ethanol is drastically increased with the effect of WO$_3$ on the surface. Sensor response of WT-1 is 18-fold higher compared to pristine TiO$_2$ NRs at 200 °C. WO$_3$ plays a key role on the surface as catalyst and increases the sensor response. Also, sensor response values of WT-1 are highest against all tested gases due to catalytic effect of WO$_3$. After the identifying optimal operation temperature, concentration dependence of sensor response was investigated at 200 °C. Concentration dependence of sensor response is given in Figure 8.
Figure 6. Comparison of XRD patterns of FTO substrate, 50 nm thick WO₃ thin film, and WT-3 sample.

Figure 7. Sensor responses of samples at constant concentration against all tested gases at a) 150 °C, b) 200 °C, and c) 250 °C.
The sensing performances of aromatic compounds such as toluene and xylene change by increasing amount of loaded WO$_3$-layer on the TiO$_2$ NRs as seen in Figures 8a and 8b. Sensing performances of pristine TiO$_2$ NRs are similar toward 1200 ppm toluene (sensor response = 0.2) and 200 ppm xylene (sensor response = 0.22) and decrease linearly by decreasing concentration of the aromatic compounds. The best sensing responses of aromatic compounds were shown by WT-1 sensor. Moreover, WT-1 sensor has saturated by increasing of concentration as clearly seen in xylene sensing performance. At low concentrations, the sensor response increases rapidly against xylene and changes slowly by increasing concentration after 100 ppm. The sensor response against aromatic compounds of WT-2 less than WT-1. Moreover, WT-3 sensor could not sense toluene and xylene. Fabricated sensors show good linear characteristics in a certain concentration range of ethanol as seen in Figure 8c. Sensor response value increases with the increment of ethanol concentration. Figure 8d shows sensor response of samples against different relative humidity concentrations at 200 °C. WT-1 sample exhibited the highest sensor response at every concentration of relative humidity.

The investigation of concentration dependence of sensor response demonstrate that all sensors are most sensitive against ethanol molecules at optimal operation temperature. Sensor response of all samples against 1850 ppm ethanol and different ethanol concentrations for WT-1 sample at 200 °C are given in Figure 9.

It’s clear that the signal returns to baseline after turning off the ethanol and purging with dry air. WO$_3$ modified TiO$_2$ NRs heterostructures showed enhanced sensor properties compared to the pristine TiO$_2$ NRs sensor. Sensing mechanisms of MOX sensors that are composed of only one type of materials have been studied and well explained in the literature [57,58]. Enhanced sensor properties can be attributed to the catalytic effect of WO$_3$. In this case, WO$_3$ plays a role as a catalyst material in the reaction between analyte gas and TiO$_2$. If the surface coverage of the WO$_3$ increase, the catalytic role of the WO$_3$ turns into a sensing layer, so a lower sensor performance generally is observed [59]. In Figure 3, SEM data also clarifies more coverage on the surface for WT-2 and WT-3. Previous works have also reported the enhanced sensor properties due to the catalytic role in heterostructures [17, 60-62]. WT-1 sample exhibited enhanced ethanol response than others and its concentration dependence sensor response performance was illustrated separately in Figure 9b. During the exposure, the response increased rapidly, then the rate of increment stopped and slightly declined to reach the saturation.
While purging the sensor, the response decreases rapidly and reaches baseline. Response times ($t_{90\text{ res}}$) of WT-1 sensor are 6 min for each ethanol concentrations. The sensor showed a very stable sensing characteristic against ethanol. On the other hand, recovery times ($t_{90\text{ rec}}$) of WT-1 sensor are 15, 14, 8, and 6 min for 1850, 900, 450, and 225 ppm ethanol, respectively. These time values are better than the ones in our previous ethanol sensor studies [22,50].

SMO materials such as TiO$_2$ and WO$_3$ have oxygen deficiencies on crystalline surface due to their specific stoichiometry. As a result of this condition, free electrons appear in the conduction band of SMO material. Therefore, this type of semiconductors is named as n-type semiconductor. Gas sensing mechanism of n-type SMO materials generally can be explained with oxygen adsorption on the surface as given in Figure 10. When the n-type SMO was exposed to ambient, oxygen molecules in the air would be adsorbed on the surface of SMO with capturing by charge carriers (free electrons) (Figure 10a). Decrease in number of charge carriers leads to appearance of depletion layer between the grain boundaries that limits the electron transfer. Therefore, the depletion layer width and contact barrier height between two adjacent grains will be increased by the remaining number of oxygen molecules. The higher contact barrier leads to lower conductance of n-type SMO. When n-type SMO material is exposed to reducing gas molecules, these molecules react with the preadsorbed oxygen molecules (Figure 10b). Then, the depletion layer width and contact barrier height between two adjacent grains decreases again. As a result, this reaction leads to increasing of n-type SMO materials conductance [63].

When there is contact formed between TiO$_2$ and WO$_3$, these two different n-type SMO materials behave as a new sensing material named as n-WO$_3$/n-TiO$_2$ heterostructure, as shown in Figure 11. Because Fermi levels of TiO$_2$ is higher...
than that of WO₃, the electrons are transferred from conduction band of TiO₂ to the conduction band of WO₃ (Figure 11a). This process would continue until equalising of the Fermi level between WO₃ and TiO₂ occurs. The formation of n-n-type heterostructure leads to the creation of an electron depletion layer in TiO₂ and an electron accumulation layer in WO₃ (Figure 11b). The accumulation layer of WO₃ would be enhanced oxygen adsorption in air ambient [40,48-50,64].

4. Conclusion
WO₃/TiO₂ heterostructures were fabricated to investigate VOCs sensing performance. According to morphological characterisation, WO₃ uniformly covered the entire highly ordered TiO₂ NRs surface. XRD investigation shows that TiO₂ NRs was grown on rutile phase and was highly aligned along the [001] direction. XRD peaks of WO₃ on samples did not exist due to their small amounts. However, further investigation illustrated that WO₃ will grow in monoclinic phase with the thermal oxidation method. TiO₂ and WO₃/TiO₂ heterostructures were tested against VOCs such as toluene, xylene, acetone and ethanol, and relative humidity. It was observed that n-n-type WO₃/TiO₂ heterostructure advanced the sensor performance of TiO₂ NRs against almost all tested gases, except acetone, which is not detected with any sensors. WT-1 sensor showed the best sensor performance compared to TiO₂, WT-2 and WT-3 sensors. Ethanol sensing response of WT-1 sensor was 18-fold higher than pristine TiO₂ NRs at 200 °C. The enhanced gas sensor performance of WO₃/TiO₂ heterostructure is attributed to n-n type heterostructure formation that leads to the formation of depletion and accumulation layers. According to our findings, n-WO₃/n-TiO₂ heterostructures have a high potential for ethanol sensor applications.

References
1. Cui P, Schito G, Cui Q. VOC emissions from asphalt pavement and health risks to construction workers. Journal of Cleaner Production 2020; 244: 118757.
2. Liu Y, Shao M, Fu L, Lu S, Zeng L et al. Source profiles of volatile organic compounds (VOCs) measured in China: part I. Atmospheric Environment. 2008; 42 (25): 6247-6260.
3. Manisalidis I, Stavropoulou E, Stavropoulos A, Bezirtzoglou E. Environmental and health impacts of air pollution: a review. Frontiers in Public Health 2020; 8.
4. Nabizadeh R, Soroshian A, Delikhoon M, Baghaz AN, Golbaz S et al. Characteristics and health effects of volatile organic compound emissions during paper and cardboard recycling. Sustainable Cities and Society 2020; 56: 102005.
5. Pekey B, Yılmaz H. The use of passive sampling to monitor spatial trends of volatile organic compounds (VOCs) at an industrial city of Turkey. Microchemical Journal 2011; 97 (2): 213-219.
6. Xie Y, Berkowitz CM. The use of positive matrix factorization with conditional probability functions in air quality studies: an application to hydrocarbon emissions in Houston, Texas. Atmospheric Environment 2006; 40 (17): 3070-3091.
7. Buszewski B, Kęsy M, Ligot T, Amann A. Human exhaled air analytics: biomarkers of diseases. Biomedical Chromatography. 2007; 21 (6): 553-566.
8. Kim K-H, Jahan SA, Kabir E. A review of breath analysis for diagnosis of human health. Trends in Analytical Chemistry 2012; 33: 1-8.
9. Popov TA. Human exhaled breath analysis. Annals of Allergy, Asthma & Immunology 2011; 106 (6): 451-456.
10. Jones A. Excretion of low-molecular weight volatile substances in human breath: focus on endogenous ethanol. Journal of Analytical Toxicology 1985; 9 (6): 246-250
11. Blohm A, Sieburg A, Popp J, Frosch T. Detection of gas molecules by means of spectrometric and spectroscopic methods. Advanced Nanostructures for Environmental Health: Elsevier; 2020. p. 251-294
12. Cernosek T, Eckert KE, Carter DO, Perrault KA. Volatile organic compound profiling from postmortem microbes using gas chromatography–mass spectrometry. Journal of Forensic Sciences 2020; 65 (1): 134-143
13. Elosúa C, Bariáin C, Matías IR, Arregui FJ, Luquin A et al. Volatile alcoholic compounds fibre optic nanosensor. Sensors and Actuators B: Chemical 2006; 115 (1): 444-449.
14. Guha P, Santra S, Gardner J. Integrated CMOS-based sensors for gas and odor detection. Semiconductor Gas Sensors: Elsevier; 2020. p. 465-487.
15. Mirzaei A, Leonardi S, Neri G. Detection of hazardous volatile organic compounds (VOCs) by metal oxide nanostructures-based gas sensors: a review. Ceramics international 2016; 42 (14): 15119-15141.
16. Sureshkumar N, Dutta A. Environmental gas sensors based on nanostructured thin films. Multilayer thin films-versatile applications for materials engineering: IntechOpen; 2020.
17. Alev O, Küçüklü, Çakurlar Ç, Büyükköse S, Öztürk ZZ. Gas sensing properties of p-Co$_3$O$_4$/n-TiO$_2$ nanotube heterostructures. Sensors 2018; 18 (4): 956.
18. Alev O, Sarıca N, Özdemir O, Arslan LÇ, Büyükköse S et al. Cu-doped ZnO nanorods based QCM sensor for hazardous gases. Journal of Alloys and Compounds 2020; 826: 154177.
19. Fu Z, Zhang G, Tang Z, Zhang H. Preparation and application of ordered mesoporous metal oxide catalytic materials. Catalysis Surveys from Asia 2020; 24 (1): 38-58.
20. Lee J-H, Mirzaei A, Kim J-Y, Kim J-H, Kim HW et al. Optimization of the surface coverage of metal nanoparticles on nanowires gas sensors to achieve the optimal sensing performance. Sensors and Actuators B: Chemical 2020; 302: 127196.
21. Sarıca N, Alev O, Arslan LÇ, Öztürk ZZ. Characterization and gas sensing performances of noble metals decorated CuO nanorods. Thin Solid Films 2019; 685: 321-328.
22. Şennik E, Alev O, Öztürk ZZ. The effect of Pd on the H$_2$ and VOC sensing properties of TiO$_2$ nanorods. Sensors and Actuators B: Chemical 2016; 229: 692-700.
23. Alev O, Şennik E, Kilinc N, Öztürk ZZ. Gas sensor application of hydrothermally growth TiO$_2$ nanorods. Procedia Engineering 2015; 120: 616-620.
24. Maziarz W, Kusior A, Trencezk-Zajac A. Nanostructured TiO$_2$-based gas sensors with enhanced sensitivity to reducing gases. Beilstein Journal of Nanotechnology 2016; 7 (1): 1718-1726.
25. Şennik E, Kilinc N, Ozturk ZZ. Electrical and VOC sensing properties of anatase and rutile TiO$_2$ nanotubes. Journal of Alloys and Compounds 2014; 616: 89-96.
26. Seo M-H, Yuasa M, Kida T, Kannura Y, Huh J-S et al. Gas sensor using noble metal-loaded TiO$_2$ nanotubes for detection of large-sized volatile organic compounds. Journal of the Ceramic Society of Japan 2011; 119 (1395): 884-889.
27. Teleki A, Pratinsis SE, Kalyanasundaram K, Gouma P. Sensing of organic vapors by flame-made TiO$_2$ nanoparticles. Sensors and Actuators B: Chemical 2006; 119 (2): 683-90.
28. Alev O, Şennik E, Öztürk ZZ. Improved gas sensing performance of p-copper oxide thin film/n-TiO$_2$ nanotubes heterostructure. Journal of Alloys and Compounds 2018; 749: 221-228.
29. Avansi Jr W, Catto AC, Da Silva LF, Fiorido T, Bernardini S et al. One-dimensional V$_2$O$_5$/TiO$_2$ heterostructures for chemiresistive ozone sensors. ACS Applied Nano Materials 2019; 2 (8): 4756-1764.
30. Deng J, Wang L, Lou Z, Zhang T. Design of CuO-TiO$_2$ heterostructure nanofibers and their sensing performance. Journal of Materials Chemistry A 2014; 2 (24): 9030-9034.
31. Lyson-Sypien B, Kusior A, Rekas M, Zukrowski J, Gajewska M et al. Nanocrystalline TiO$_2$/SnO$_2$ heterostructures for gas sensing. Beilstein Journal of Nanotechnology 2017; 8 (1): 108-122.
32. Wang Y, Wu T, Zhou Y, Meng C, Zhu W et al. TiO$_2$-based nanoheterostructures for promoting gas sensitivity performance: designs, developments, and prospects. Sensors 2017; 17 (9): 1971.
33. Kanda K, Maekawa T. Development of a WO₃ thick-film-based sensor for the detection of VOC. Sensors and Actuators B: Chemical 2005; 108 (1-2): 97-101.

34. Vallejos S, Khatcho V, Calderer J, Gracia I, Cané C et al. Micro-machined WO₃-based sensors selective to oxidizing gases. Sensors and Actuators B: Chemical 2008; 132 (1): 209-215.

35. Liu Y, Xie C, Li H, Chen H, Zou T, Zeng D. Improvement of gaseous pollutant photocatalysis with WO₃/TiO₂ heterojunctional-electrical layered system. Journal of Hazardous Materials 2011; 196: 52-58.

36. Prabhuh S, Nithya A, Mohan SC, Jothivenkatachalam K (editors). Synthesis, surface acidity and photocatalytic activity of WO₃/TiO₂ nanocomposites – an overview. Materials Science Forum; 2014; 781: 63-78.

37. Tang K, Zhang Y, Shi Y, Cui J, Shu X et al. Fabrication of WO₃/TiO₂ core-shell nanowire arrays: structure design and high electrochromic performance. Electrochimica Acta 2020; 330: 135189.

38. Depero L, Ferroni M, Guidi V, Marca G, Martinelli G et al. Preparation and micro-structural characterization of nanosized thin film of TiO₂-WO₃ as a novel material with high sensitivity towards NO₂. Sensors and Actuators B: Chemical 1996; 36 (1-3): 381-383.

39. Lee DS, Han SD, Lee SM, Huh JS, Lee DD. The TiO₂-adding effects in WO₃-based NO₂ sensors prepared by coprecipitation and precipitation method. Sensors and Actuators B: Chemical 2000; 65 (1-3): 331-335.

40. Yao Y, Yuan J, Chen X, Tan L, Gu Q et al. In situ construction and sensing mechanism of TiO₂–WO₃ composite coatings based on the semiconductor heterojunctions. Journal of Materials Research and Technology 2019; 8 (4): 3580-8358.

41. Zanetti S, Rocha K, Rodrigues J, Longo E. Soft-chemical synthesis, characterization and humidity sensing behavior of WO₃/TiO₂ nanopowders. Sensors and actuators B: Chemical 2014; 190: 40-47.

42. Meng W, Dai L, Zhu J, Li Y, Meng W et al. A novel mixed potential NH₃ sensor based on TiO₂@ WO₃ core-shell composite sensing electrode. Electrochimica Acta 2016; 330: 302-310.

43. Zappa D, Galstyan V, Kaur N, Munasinghe Arachchige HMM, Sisman O, Comini E. Metal oxide -based heterostructures for gas sensors- a review. Analytica Chimica Acta 2018; 1039: 1-23.

44. Walker JM, Akbar SA, Morris PA. Synergistic effects in gas sensing semiconducting oxide nano-heterostructures: A review. Sensors and Actuators B: Chemical 2019; 286: 624-640.

45. Moseley PT. Progress in the development of semiconducting metal oxide gas sensors: a review. Measurement Science and Technology 2017; 28 (8): 082001.

46. Feng X, Shankar K, Varghese OK, Paulose M, Latempa TJ et al. Vertically aligned single crystal TiO₂ nanowire arrays grown directly on transparent conducting oxide coated glass: Synthesis details and applications. Nano Letters 2008; 8 (11).

47. Astinchap B, Moradian R, Gholami K. Effect of sputtering power on optical properties of prepared TiO₂ thin films by thermal oxidation of sputtered Ti layers. Materials Science in Semiconductor Processing 2017; 63: 169-175.

48. Xiao G, Shi C, Li L, Zhang Z, Ma C et al. A 200-nm length TiO₂ nanorod array with a diameter of 13 nm and areal density of 1100 µm⁻² for efficient perovskite solar cells. Ceramics International 2017; 43 (15): 12534-12539.

49. Altomare M, Nguyen NT, Hejazi S, Schmuki P. A Cocatalytic electron- transfer cascade site- selectively placed on TiO₂ nanotubes yields enhanced photocatalytic H₂ evolution. Advanced Functional Materials 2018; 28 (2): 1704259.

50. Şennik E, Soysal U, Öztürk ZZ. Pd loaded spider-web TiO₂ nanowires: fabrication, characterization and gas sensing properties. Sensors and Actuators B: Chemical 2014; 199: 424-432.

51. Lin CW, Huang KL, Chang KW, Chen JH, Chen KL et al. Ultraviolet photodetector and gas sensor based on amorphous In–Ga–Zn–O film. Thin Solid Films 2016; 618: 73-76.

52. Wu CH, Jiang GJ, Chang KW, Lin CW, Chen KL. Highly sensitive amorphous In–Ga–Zn–O films for ppb-level ozone sensing: effects of deposition temperature. Sensors and Actuators B: Chemical 2015; 211: 354-358.

53. Lai CW, Sreekantan S. Preparation of hybrid WO₃-TiO₂ nanotube photoelectrodes using anodization and wet impregnation: improved water-splitting hydrogen generation performance. International Journal of Hydrogen Energy 2013; 38 (5): 2156-2166.

54. Banerjee AN. The design, fabrication, and photocatalytic utility of nanostructured semiconductors: focus on TiO₂-based nanostructures. Nanotechnology, Science and Applications 2011; 4: 35.

55. Suryawanshi H, Patil D. Synthesis of nanostructure TiO₂ nanorod array on FTO substrate using hydrothermal method and its photocatalytic activity. International Journal for Research in Applied Science & Engineering Technology 2018; 6 (4): 48-53.

56. Meng X, Shin DW, Yu SM, Park MH, Yang C et al. Formation mechanism of rutile TiO₂ rods on fluorine doped tin oxide glass. Journal of Nanoscience and Nanotechnology 2014; 14 (11): 8839-8844.
57. Liu Y, Li G, Mi R, Deng C, Gao P. An environment-benign method for the synthesis of p-NiO/n-ZnO heterostructure with excellent performance for gas sensing and photocatalysis. Sensors and Actuators B: Chemical 2014; 191: 537-544.

58. Miller DR, Akbar SA, Morris PA. Nanoscale metal oxide-based heterojunctions for gas sensing: a review. Sensors and Actuators B: Chemical 2014; 204: 250-272.

59. Liu L, Guo C, Li S, Wang L, Dong Q et al. Improved H2 sensing properties of Co-doped SnO2 nanofibers. Sensors and Actuators B: Chemical 2010; 150 (2): 806-810.

60. Wöllenstein J, Burgmair M, Plescher G, Sulima T, Hildenbrand J et al. Cobalt oxide based gas sensors on silicon substrate for operation at low temperatures. Sensors and Actuators B: Chemical 2003; 93 (1): 442-448.

61. Liu PF, Yang S, Zheng LR, Zhang B, Yang HG. Electrochemical etching of α-cobalt hydroxide for improvement of oxygen evolution reaction. Journal of Materials Chemistry A 2016; 4 (24): 9578-9584.

62. Kohl D. Function and applications of gas sensors. Journal of Physics D: Applied Physics 2001; 34 (19): R125-R49.

63. Xu C, Tamaki J, Miura N, Yamazoe N. Grain size effects on gas sensitivity of porous SnO2-based elements. Sensors and Actuators B: Chemical 1991; 3 (2): 147-155.

64. Ali H, Ismail N, Hegazy A, Mekewi M. A novel photoelectrode from TiO2-WO3 nanoarrays grown on FTO for solar water splitting. Electrochimica Acta 2014; 150: 314-319.