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The effect of deposition time on the structural, morphological and H_2S gas sensing properties of the V_2O_5 nanostructures deposited by hydrothermal method

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Abstract
V_2O_5 nanostructures were successfully deposited on glass substrates by hydrothermal method at 180 °C for the deposition times of 4, 6, 8, 10 h. The effect of deposition time on the structural, morphological, compositional and H_2S gas sensing properties of the nanostructures were investigated by XRD, SEM, EDAX and gas measurement system, respectively. The XRD and SEM studies indicated that the nanostructures had polycrystalline nature with monoclinic phase of V_2O_5 and the structural and morphological properties of the nanostructures depended on the deposition time. The sensing measurements of the sensors were made based on temperature and gas concentration. The sensors exhibited high responses towards 50 ppm H_2S gas concentration at operating temperature of 145 °C. In addition, the sensors showed acceptable responses at temperatures below the operating temperature of 50 °C. It was seen that the gas sensing properties of the nanostructure deposited for 6 h deposition time were better than others.

1 Introduction

Air pollution has a serious toxicological effect on human health. Sensitive, efficient and rapid sensing of gases harmful to human health is an urgent need. Therefore, great efforts are being made to develop new detection technologies that will replace available methods such as liquid chromatography (LC) and gas chromatography (GC). Especially, metal oxide gas sensors have become attractive devices in gas sensor technology, because of their high flexibility and stability, low cost, feasibility in detecting various gases, simplicity of operation. Amongst a large number of metal oxides, vanadium pentoxide (V_2O_5) has attracted considerable interest over the years due to its wide range of technological applications.

V_2O_5 has excellent properties such as high thermal and chemical stability, direct optical band gap (2.2–2.7 eV), multiple valency, excellent thermoelectric properties [1–3]. V_2O_5 is an n-type semiconducting oxide. When V_2O_5 is exposed to the reducing gas, the V^{5+} ions reduce to V^{4+} and the electrical conductivity of V_2O_5 increases. In addition, V^{5+} ions have d0 electron configuration and the ions form active sites. These active sites are able to catalyze reactions and adsorb gaseous molecules. With these properties, V_2O_5 is a promising material for microelectronic, electrochemical, window for solar cells, gas sensors and optoelectronic devices [1, 4–6].

V_2O_5 nanostructures can be prepared by different methods such as vacuum based and solution based. Nevertheless, solution based methods have taken the researcher's attention, due to parameters such as low cost, repeatability, simplicity, non-toxic. V_2O_5 nanostructures are prepared by solution

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based methods such as co-precipitation, micro-emulsion, chemical bath deposition and hydrothermal method. Among these, hydrothermal method is the most familiar and widely used for the synthesis of V_2O_5 nanostructures with tailored morphology and sizes. Hydrothermal method is a chemical process. Thus, the solution concentration, reaction temperature and time are vital parameters, which affect the characteristics properties of the V_2O_5 nanostructures [7, 8].

As a result of decomposition of organic materials in anaerobic environment, H_2S gas is naturally produced. H_2S gas is found in large quantities in oil and natural gas industries, paper milling, sewage treatment, and landfills [9, 10]. H_2S gas is colorless, corrosive, flammable, extremely toxic. It is potentially lethal in concentrations as low as few parts per million (ppm). Frequently, industrial workers are at risk of exposure to H_2S gas and even gas explosion. Therefore, new and superior materials are needed to prevent the fatal risks of H_2S gas and to provide higher performance with low power consumption sensors [9, 11].

There are very limited number of reports about H_2S gas sensing properties of V_2O_5 nanostructures. In this study, we mainly focused on producing V_2O_5 nanostructures with hydrothermal method and their H_2S gas sensing properties. In order to achieve a better understanding of the influence of the deposition time on the structural, morphological, compositional and H_2S gas sensing properties of the nanostructures, V_2O_5 nanostructures were successfully deposited on glass substrates by hydrothermal method at 180 °C for the deposition times of 4, 6, 8, 10 h. The sensing measurements of the sensors were made based on temperature and gas concentration. This study not only throws some light on the fundamental understanding of the H_2S gas sensing for V_2O_5 nanostructures but also provides a promising approach to achieve efficient detection of H_2S gas at low operating temperature.

2 Experimental methods

2.1 Deposition of V_2O_5 nanostructures

V_2O_5 nanostructures were successfully deposited on glass substrates by hydrothermal method at 180 °C for the deposition times of 4, 6, 8, 10 h. For deposition V_2O_5 nanostructures, ammonium metavanadate (NH_4VO_3—99%, Sigma-Aldrich) was used as vanadium source. 0.1 M NH_4VO_3 solution was prepared in deionized water for deposition of V_2O_5 nanostructures. The pH of this solution was adjusted to pH 4 using 0.3 M oxalic acid ($H_2C_2O_4 \geq 99\%$, Sigma-Aldrich) and the mixture solution was stirred with a magnetic stirrer at room temperature for 30 min. Then, the mixture solution was transferred into a 50 mL Teflon-lined autoclave. The glass substrate, which was inclined at about 45° angle to the walls of Teflon was placed into the solution (Fig. 1a). At four different deposition standby times, V_2O_5 nanostructures were deposited on glass substrates. The nanostructures produced were named SO1 (4 h), SO2 (6 h), SO3 (8 h) and SO4 (10 h).

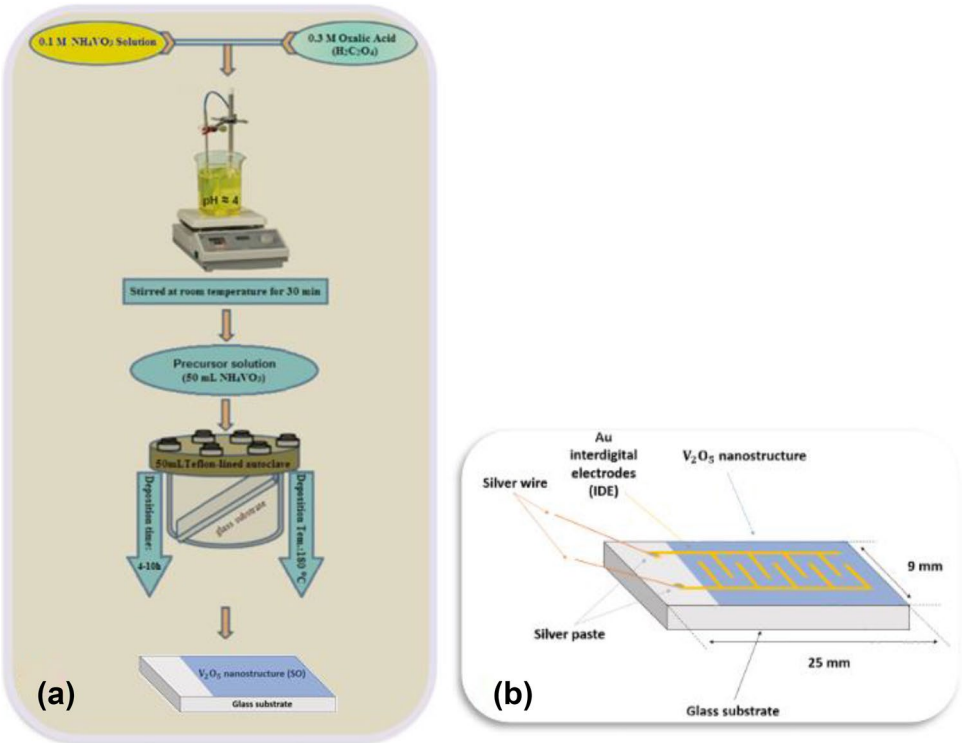

Fig. 1 Schematic diagrams of the deposition of V_2O_5 nanostructures [8] (**a**) and sensor device (**b**)

Firstly, structural and morphological characterizations of the V_2O_5 nanostructures were carried out. After then, the interdigitated (IDT) gold electrodes were coated on the nanostructures by thermal evaporation using Au metal (99.99%, Sigma-Aldrich). Finally, gas sensing measurements were tested for this structure, where the IDT electrodes are at the top (Fig. 1b). Fytronix hydrothermal device was used for deposition V_2O_5 nanostructures.

2.2 Characterization methods

To investigate deposition time effect on the structural, morphological and compositional properties of the V_2O_5 nanostructures; XRD, SEM and EDAX measurements were used. Panalytical Empyrean X-Ray Diffractometer (using Cu Kα λ = 1.5405 Å radiation with 2θ of 5°–100°, operated at 45 kV and 40 mA) for XRD measurements, a field-emission scanning electron microscope (FESEM: FEI Quanta 450 FEG, operated at an acceleration voltage of 10 kV, at high vacuum (HV) mode) for SEM measurements and an energy dispersion X-ray spectroscopy (EDS) analyzer in an FESEM system (EDAX, AMETEK Materials Analysis Division) for EDAX measurements were used.

The gas sensing properties of the nanostructure sensors were tested using a special computer-controlled measurement system, which was fully detailed in our previous paper [12]. The nanostructure sensors were evaluated by measuring the resistance change at various H_2S gas concentrations from 1 to 50 ppm and at different operating temperatures from 35 to 210 °C. The H_2S concentration and dry air flow rates were controlled by computer controlled mass flow controllers (MKS Series). This measurement system involved Keithley 2400 Source Meter, A LakeShore 325 temperature controller. The sensor response (S) was calculated using the following equation [12, 13];

$$S(\%) = \left(\frac{R_g - R_a}{R_a}\right) \times 100 \quad (1)$$

where R_a is the resistance in dry air and R_g is the resistance upon exposure the target gas in dry air.

3 Results and discussions

3.1 Structural and morphological characterization

The XRD patterns of the V_2O_5 nanostructures (SO1—4 h, SO2—6 h, SO3—8 h, SO4—10 h) are shown in Fig. 2. The XRD patterns of the nanostructures indicate the existence of monoclinic β-V_2O_5 single phase [14, JCPDS 98-015-6051] in Fig. 2. All the nanostructures have polycrystalline structure with orientation along with different planes. These planes are (001), (011), (200), (111), (103) and (020). Although the intensities and full width at half maximum (FWHM) values of these peaks changed with the deposition time, all the nanostructures had the same crystal structure. XRD patterns of the V_2O_5 nanostructures have very high and sharp peak intensities. It was determined that the crystallinity of the nanostructures was improved with deposition time up to 8 h and began to break down after 8 h deposition time.

The SEM images of the V_2O_5 nanostructures are shown in Fig. 3. The morphological properties of the nanostructures changed significantly depending on the deposition time. It was observed that the surface morphologies of the V_2O_5 nanostructures consisted of nanorods and nanoballs. V_2O_5 nanostructure (SO1—4 h) consists of one-dimensional and horizontally placed nanorods, some of these nanorods appear to be of irregular in size and shape. The nanorods are dispersed with the width almost 150–200 nm and the length almost 650–850 nm. V_2O_5 nanostructure (SO2—6 h) consists of a large number of uniform nanoballs. The nanoballs are in the range of 450–500 nm in diameter and the surfaces of the nanoballs are covered with uniform flakes. V_2O_5 nanostructure (SO3—8 h) consists of one-dimensional nanorods, which are dispersed almost perpendicular to the surface of the substrate. The width of nanorods is almost range of 50–80 nm. V_2O_5 nanostructure (SO4—10 h) consists of one-dimensional and horizontally placed nanorods, some of which these nanorods appear to be of irregular size. The nanorods are dispersed with the width almost 50–80 nm and the length almost 250–300 nm. Consequently, the deposition time played a crucial role on structural and morphological properties of the V_2O_5 nanostructures during the hydrothermal process. The compositional (EDAX) analysis V_2O_5 nanostructures (SO1—4 h, SO2—6 h, SO3—8 h, SO4—10 h) are shown in Fig. 4. EDAX analysis shows the presence of V and O elements in the nanostructures. The atomic percent values of these elements in the nanostructures were given in the inset of EDAX analysis. The presence of Si element may originate from the substrate.

3.2 Formation mechanism of nanostructures

The formation mechanism of nanorod and nanoball structures on the surface of glass substrate by hydrothermal method is presented in Fig. 5. V_2O_5 nanostructures were obtained by varying deposition time (4 h, 6 h, 8 h and 10 h). The chemical reaction is given below;

$$2NH_4VO_{3(aq)} + H_2C_2O_{4(aq)} \rightarrow V_2O_{5(s)} + CO_{2(g)} + CO_{(g)} + 2NH_4OH_{(aq)} \quad (2)$$

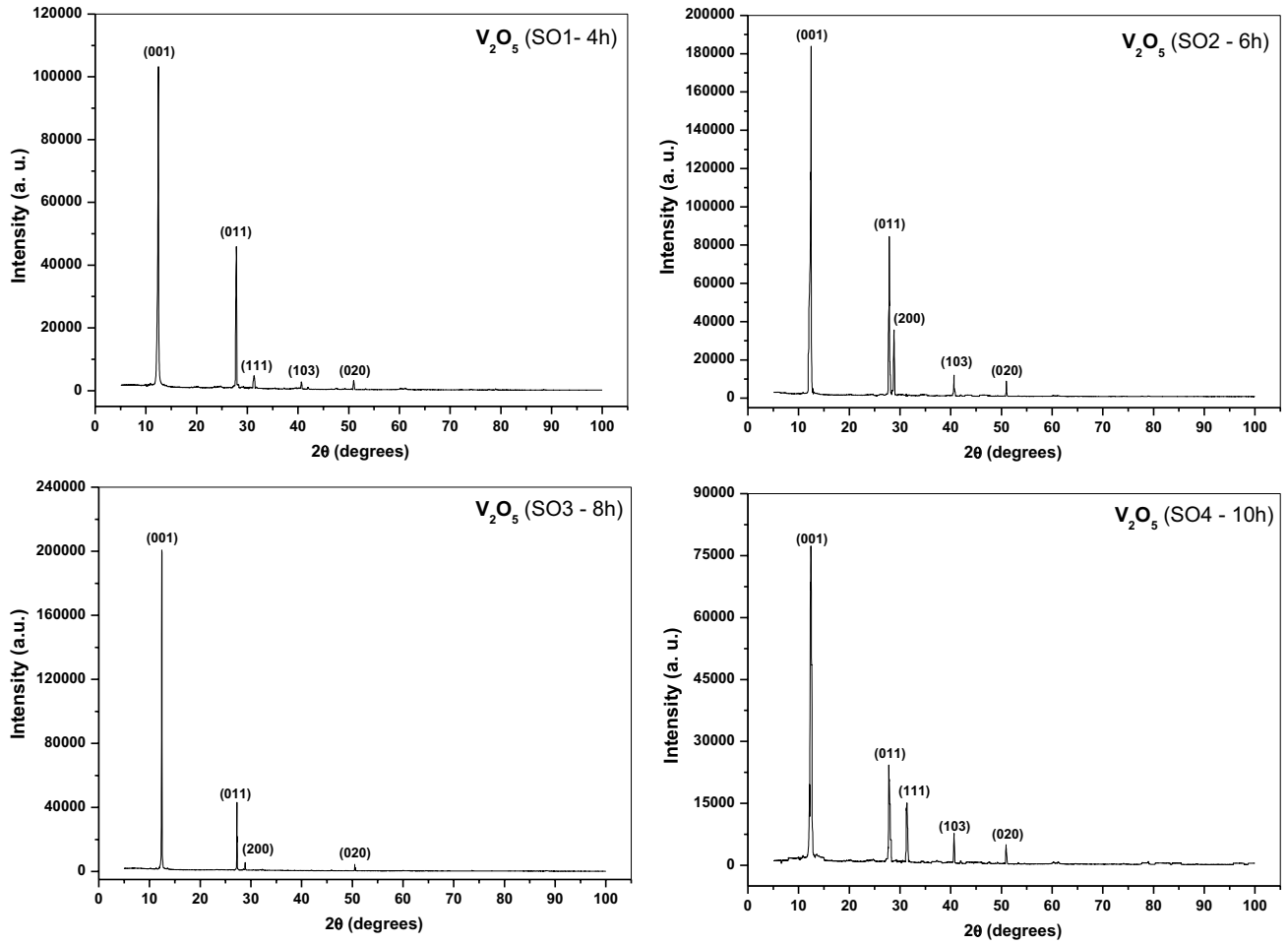

Fig. 2 The XRD patterns of V_2O_5 nanostructures (SO1—4 h, SO2—6 h, SO3—8 h, SO4—10 h)

NH_4VO_3 nucleates on the surface of glass substrate and forms V_2O_5 nanostructure. Small nanorod and nanoflake structures nucleate and grow on the surface of glass substrate. Their density, size and form vary according to the deposition time (4 h, 6 h, 8 h and 10 h).

V_2O_5 nanostructures deposited for 4 h, 8 h and 10 h were subjected to heat and pressure treatment. Initially, nanorods are formed in small size by the deposition process (in Fig. 5a). These nanorods self-assemble together to form nanorods of different sizes and shapes according to the deposition time as shown in the SEM images (SO1—4 h, SO3—8 h and SO4—10 h). V_2O_5 nanostructure deposited for 6 h was subjected to heat and pressure treatment. Initially, nanoflakes are formed in small size by the deposition process (in Fig. 5b). These nanoflakes undergo the process of recrystallization according to Ostwald ripening process [8] in which the larger particles grow at the expense of smaller particles and form V_2O_5 nanoballs. Consequently, small size nanoflakes form nanoballs with the Ostwald ripening process for 6 h deposition time under the effect of heat and pressure as shown in the SEM image (SO2—6 h).

3.3 Gas sensing measurements

To demonstrate the potential application as a gas sensor of V_2O_5 nanostructures, H_2S was chosen as the testing gas. In order to attain the optimum sensing performances of V_2O_5 nanostructure sensors, the responses of the sensors were measured over a wide range of operating temperatures (35–210 °C). Figure 6 shows the responses of V_2O_5 nanostructure sensors to 50 ppm H_2S gas at different operating temperatures. As well known, gas sensing performances of V_2O_5 nanostructure sensors are largely dependent on its operating temperature that controls the reaction kinetics, conductivity and electron mobility. It was seen from the Fig. 6 that the response of all the sensors increased with operating temperature and reached to the maximum at 145 °C. After this temperature, the response of all the sensors began to decrease. This behavior can be attributed to

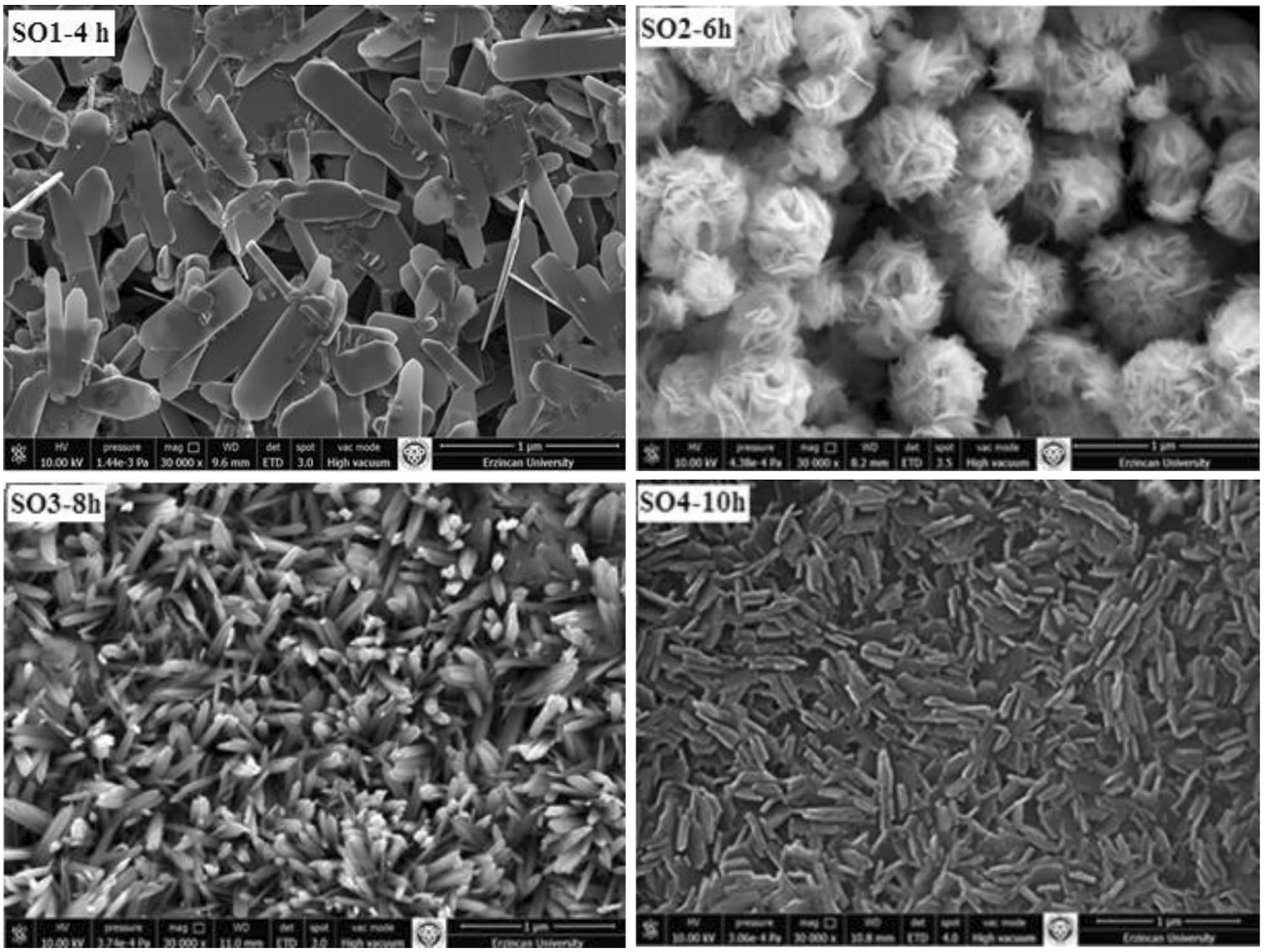

Fig. 3 SEM images of V_2O_5 nanostructures (SO1—4 h, SO2—6 h, SO3—8 h, SO4—10 h)

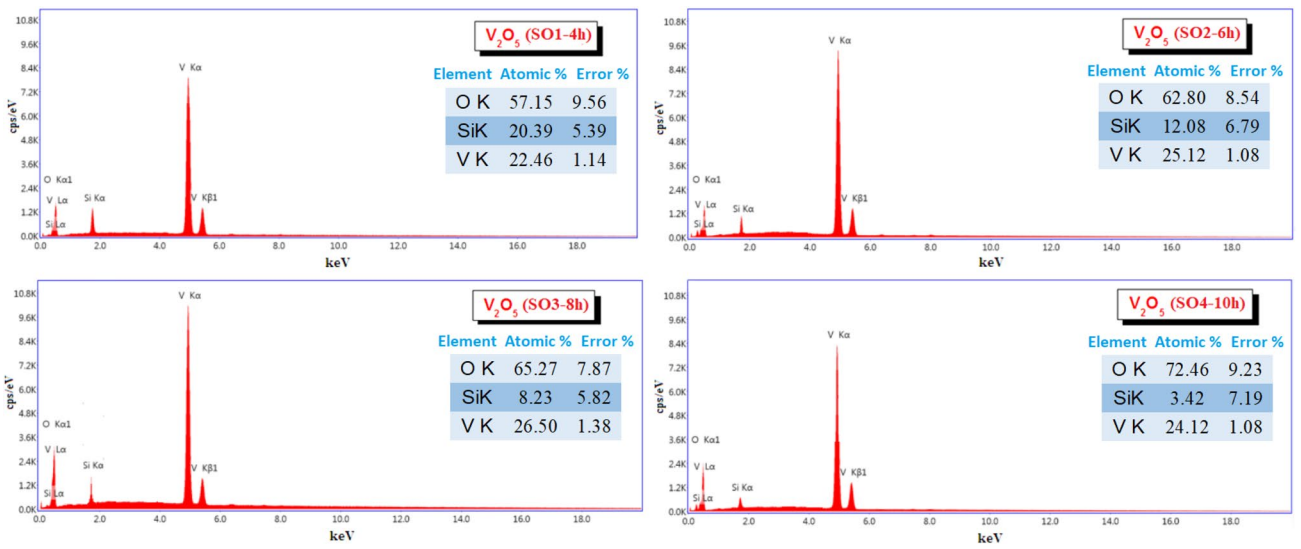

Fig. 4 EDAX analysis of V_2O_5 nanostructures (SO1—4 h, SO2—6 h, SO3—8 h, SO4—10 h)

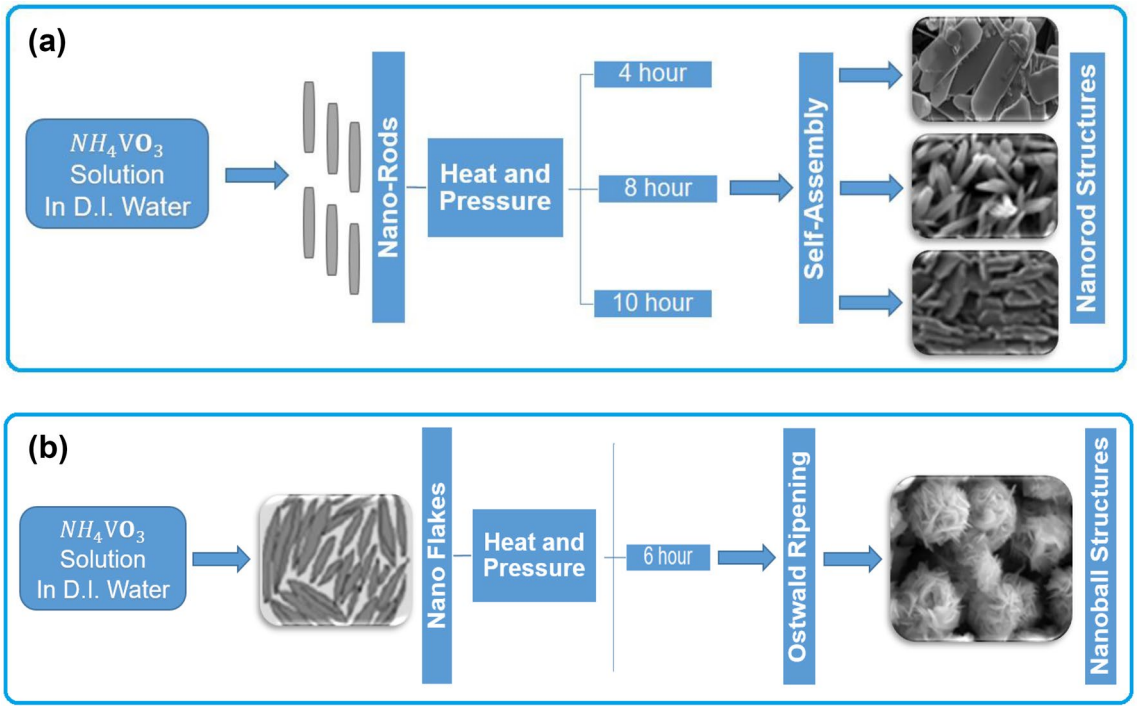

Fig. 5 The formation mechanism of nanorod (**a**) and nanoball (**b**) structures

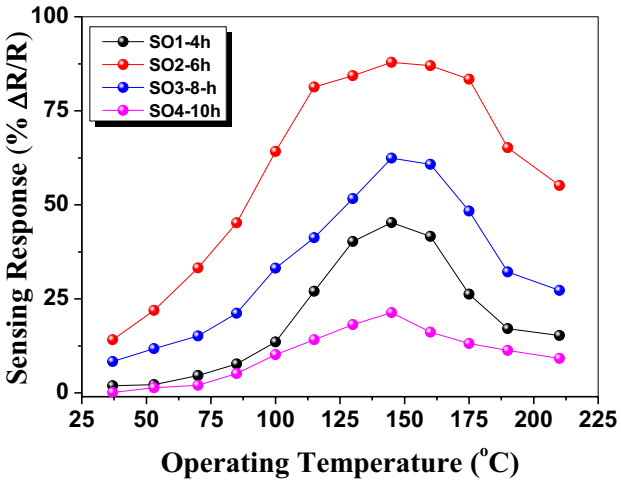

Fig. 6 The response of V_2O_5 nanostructure sensors as a function of operating temperature for constant 50 ppm H_2S gas concentration

the decomposition and the adsorption of oxygen ions on the surface of the sensor, depending on the operating temperature. The oxygen could be removed or be lost from the metal oxide materials at high temperatures. Therefore, the response of the sensor may decrease at high temperatures [13, 15]. The optimal operating temperature was found 145 °C for all the V_2O_5 nanostructure sensors. At the optimal operating temperature and 50 ppm H_2S gas concentration, the response of SO1, SO2, SO3 and SO4 sensors was calculated to be 45, 88, 62 and 21%, respectively. The maximum response was obtained for SO2 nanostructure sensor (Fig. 6 and Table 1).

Figures 7 and 8 show the dynamic gas measurements of the V_2O_5 nanostructure sensors for different gas concentrations from 1 to 50 ppm at operating temperature of 145 °C. The responses of the V_2O_5 nanostructure sensors increased with increasing gas concentrations. As is seen in Figs. 7, 8 and Table 1, SO2 nanostructure sensor has the maximum

Table 1 The results of the gas sensing measurements of the V_2O_5 nanostructure sensors at operating temperature of 145 °C

V_2O_5 nanostructure sensors	Response of sensors		Response time (s) of sensors		Recovery time (s) of sensors	
	H_2S gas concentration		H_2S gas concentration		H_2S gas concentration	
	1 ppm	50 ppm	1 ppm	50 ppm	1 ppm	50 ppm
SO1–4 h	% 5	% 45	8.6	2.2	7.6	1.3
SO2–6 h	% 13	% 88	4.5	1.4	4.5	1.4
SO3–8 h	% 8	% 62	12	2.4	9.0	2.4
SO4–10 h	% 3	% 21	12	4.3	15.0	4.4

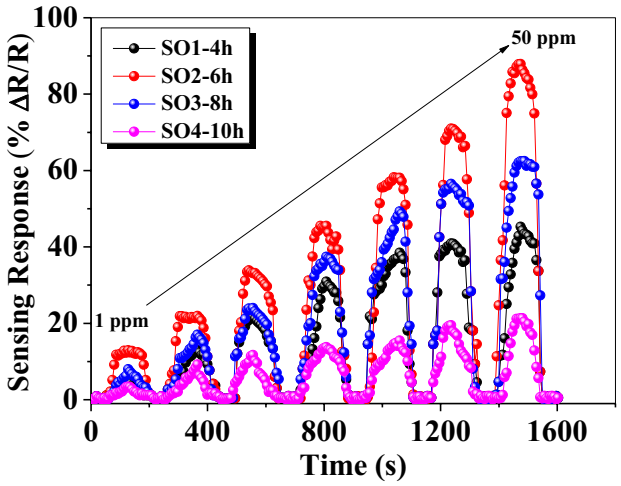

Fig. 7 The responses of the V_2O_5 nanostructure sensors exposed to 1–50 ppm of H_2S gas at operating temperature of 145 °C

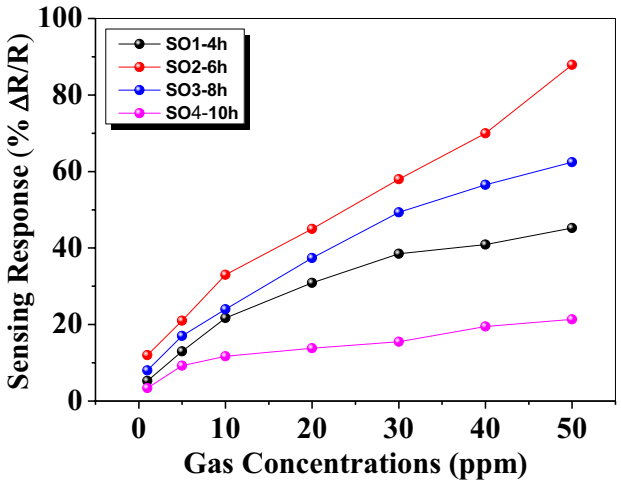

Fig. 8 The response of the V_2O_5 nanostructure sensors as a function of H_2S gas concentrations at operating temperature of 145 °C

response compared to the other sensors in the whole H_2S gas concentrations (1–50 ppm). The morphological property of the SO2 nanostructure played a crucial role in high response of the sensor. The surfaces of the nanoballs were covered with uniform flakes (in SO2) and the uniform flakes interacted better than the other nanostructures with H_2S molecules. Surface morphology has a significant impact on the gas adsorption, because the effective surface area of V_2O_5 affecting the gas adsorption increases the sensitivity of the sensor. Thus, it is estimated that adaptation of the effective surface area may lead to a significant improvement in sensitivity of the sensor [16]. Schneider et al. reported that V_2O_5 thin films exhibited good response towards hydrogen (5–300 ppm), methane and propane (50–3000 ppm) gases within temperature range of 448–473 K [4]. Also, Schneider et al. presented a short review of the V_2O_5 based resistive gas sensors. Dhayal Raj et al. reported that the sensing behavior of V_2O_5 nanorods was monitored for ammonia and ethanol at different ppm levels [3].

A potential gas sensing mechanism of resistive gas sensors can be proposed as follows: First, the electrical behavior is sufficiently modified by adsorption and desorption of oxygen species from ambient air on the surface. When exposed to air, the surfaces of the V_2O_5 nanostructures will adsorb some oxygen molecules. The electrical properties of the V_2O_5 nanostructures change with the oxygen adsorption. The adsorbed oxygen molecules transform into oxygen ions (O_2^-, O^-, O^{2-}) depending on the temperature by capturing free electrons from conduction band of the V_2O_5 nanostructures. Then, depletion layer is formed on the surface regions, causing an increase in the resistance of the V_2O_5 nanostructures [17, 18]. When the sensing surface is exposed to H_2S gas, the adsorption of H_2S molecules as reducing gas react with the oxygen ions on the surface of the sensor [9, 19]. The reaction is given by [9, 19];

$$H_2S_{(gas)} + 3O^-_{(ads)} \rightarrow H_2O_{(gas)} + SO_{2(gas)} + 3e^- \quad (3)$$

Releasing electrons back to conduction band of the V_2O_5 decreases the widths of the depletion layer. Consequently, a decrease in the resistance of the V_2O_5 nanostructures is observed. Li et al. [20, p. 173] and Mirzaei et al. [9, p. 318] schematically reported the H_2S gas sensing mechanism of metal oxide based sensors.

The response time and recovery time are two important criteria to judge the gas sensing performance of the gas sensors. The response time and recovery time were defined as the times to reach 90% of the resistance change when the target gas (H_2S) and carrier gas (air) were injected into the

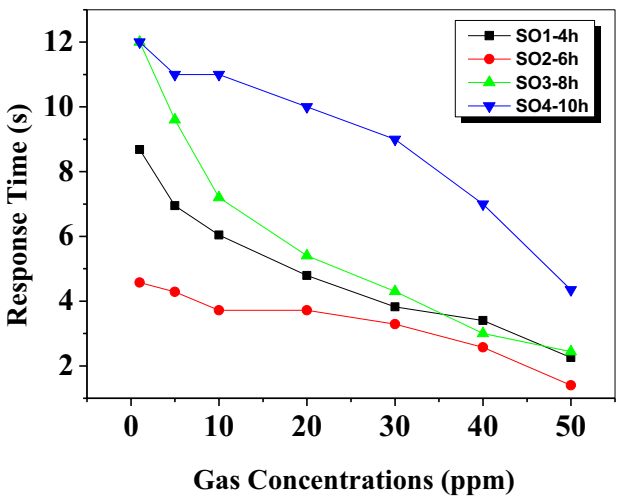

Fig. 9 The response time of the V_2O_5 nanostructure sensors as a function of H_2S gas concentrations at operating temperature of 145 °C

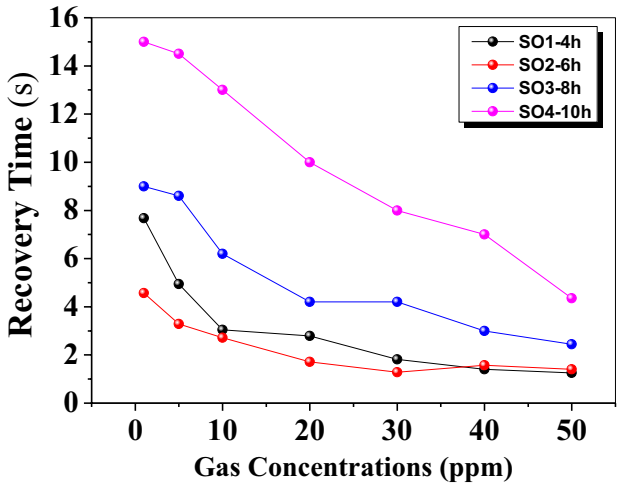

Fig. 10 The recovery time of the V_2O_5 nanostructure sensors as a function of H_2S gas concentrations at operating temperature of 145 °C

chamber, respectively. Figures 9 and 10 show the response time and recovery time of the V_2O_5 nanostructure sensors as a function of gas concentration at operating temperature of 145 °C, respectively. As seen Figs. 9, 10, and Table 1, SO2 nanostructure sensor has the fastest response time and recovery time compared to other sensors. The response time and recovery time for 1 ppm H_2S gas were obtained 4.5 s for SO2 nanostructure sensor (Table 1). The time values are considered fast compared with reported sensors in the literature [6, 9, 11, 20].

4 Conclusions

V_2O_5 nanostructures were successfully deposited on glass substrates by hydrothermal method at 180 °C for the deposition times of 4 (SO1), 6 (SO2), 8 (SO3), 10 (SO4) h. The effect of deposition time on the structural, morphological and H_2S gas sensing properties of the V_2O_5 nanostructures were investigated. The XRD patterns of the nanostructures indicate the existence of monoclinic β-V_2O_5 single phase and have very high and sharp peak intensities. The morphological properties of the nanostructures changed significantly depending on the deposition time. It was determined that the surface morphologies of the V_2O_5 nanostructures consisted of nanorods and nanoballs. The H_2S gas sensing properties of the V_2O_5 nanostructures including sensing response, response time and recovery time were studied as a function of temperature and gas concentration. All the sensors exhibited high sensing responses, low response and recovery times when exposed to H_2S gas concentration in the range of 1–50 ppm at operating temperature of 145 °C. It was seen that the gas sensing properties of the SO2—6 h were better than others. The sensing response of the SO2 nanostructure sensor to 1 ppm and 50 ppm H_2S gas was 13%, 88% at operating temperature (145 °C), respectively. The response and recovery time of the SO2 nanostructure sensor to 1 ppm H_2S gas were as low as 4.5 s and 4.5 s at operating temperature (145 °C), respectively. Consequently, the results suggest that the V_2O_5 nanostructures deposited by hydrothermal method can be a promising sensing material for high performance H_2S gas sensor, which can be used in the oil and natural gas industries.

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