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New generation of α-MnO_2 nanowires @PDMS composite as a hydrogen gas sensor

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Abstract
New hydrogen gas sensor has been prepared by α-MnO_2 nanowires in polydimethylsiloxane matrix. For this purpose, the high aspect ratio α-MnO_2 nanowires has been prepared by the aid of hydrothermal method and then dispersed into poly-dimethyl siloxane polymer media. For gas sensing, the samples have been exposed under different gas concentrations from 0 to 5%. The sensor responses have been examined by normalized ellipsometric parameter with respect to the chamber filled with N_2 Gas. Our results indicate linear behavior of resonance wavelength in ellipsometric parameter as a function of gas concentrations which can open a new insight for the sample's capability to hydrogen gas sensing applications.

1 Introduction

Optically hydrogen gas sensors have been extensively studied due to the fast data recording and easy signal transportation. These sensors can be designed, and fabricated as miniaturized and multi-wavelengths heads to use in industrial fields such as rocket propellant, metallurgy, home appliances, and factory. These optical sensors can be classified into fields such as fiber optic sensors [1], interferometers [2], semiconductor [3], MEMS [4], surface state waves [5] and also thin absorptive film such as palladium (Pd) which can absorb 900 times of its volume get much attention in this field [6, 7].

In spite of metal thin films, the metal oxide gas sensors have been widely used in recent years. Among these metal oxide classes, manganese dioxide (MnO_2) which depends on its crystalline phases can be used as an efficient energy storage in batteries [8], ion-exchanger [9], oxidizer [10] and also absorber [11]. The latest usage of these structures drift scientists to design and construct gas sensors such as hydrogen gas sensors [12]. Use of manganese dioxide components as a hydrogen gas sensor has been reported by many researchers because of its cost and thermal stability characteristics. Based on these reports, the side-heated hydrogen gas sensor is based on high aspect ratio nanowires [13], potentiometric-type H_2 gas sensor [14], and MnO_2 nanoflake sensor [15].

For this purpose, compared to its bulk, powder or thin films structures, nanostructures of them as nanoparticles or one-dimensional nanostructures such as nanowires has attracted extensive attention because of the high surface to volume ratio [16]. Different structural forms of MnO_2 can be produced via various methods. The famous of these structures are α, β, γ and δ–MnO_2, which differ from each other by the location of the MnO_6 octahedron. This displacement provides different void spaces in MnO_2 structures [17].

Controlling the parameters of synthesis methods will affect the dimension and size of the MnO_2 phases. One-dimensional structure of MnO_2, as a critical factor, can provide various properties for individual applications. Therefore, well-controlled size and dimensionality of MnO_2 are very important. Although α-MnO_2 nanostructures can be used as catalyst absorbents and Li+-related batteries [18], using these materials as a new generation of gas sensor has been examined for the first time in this report.

2 Experimental procedure

α-MnO_2 nanowires have been prepared by hydrothermal method using [$MnSO_4 \cdot H_2O$], [$(NH_4)_2S_2O_8$] and [$(NH_4)_2SO_4$] as the starting materials. 0.02 mol of $MnSO_4 . H_2O$ and 0.02 mol of $(NH_4)_2S_2O_8$ were dissolved in 42 ml

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of deionized water. Then 0.08 mol of $(NH_4)_2SO_4$ in 42 ml of deionized water was added to the initial solution. After mixing them with a stirrer at about 30 min, it was transferred into a Teflon-lined stainless steel autoclave and then reacted for 12 h at 120 °C. After this, the precipitation was rinsed for five times with deionized water and ethanol and finally dried at 80 °C for 12 h.

Powder X-ray diffraction (D8-Advance–Bruker using Cu Kα radiation with a step of 0.02 °/s) measurements were employed to identify the crystal structure of the α-MnO_2 samples. A field-emission scanning electron microscope (MIRA3TESCAN-XMU) was used to find out the morphology and the dimensions of our nanowire samples. Figure 1 shows the image of as-prepared α-MnO_2 sample. After that, our optical composite has been prepared by polydimethylsiloxane (PDMS) polymer (Sylgard 184) from Dow Corning was used. It consists of a siloxane base and a curing agent which must be mixed in 10:1 volumetric ratio. α-MnO_2 NWs were mixed with the PDMS base at about 0.05 wt%. The dispersion of NWs has been done in two steps; first the mixture of PDMS base and α-MnO_2 NWs was sonicated for an hour at room temperature and then it was mixed mechanically by a DC motor for 30 min. Before the final minute of mixing, the curing agent was added to the PDMS base in 1:10 volumetric ratio. Then the composite has been poured into a mold and it was placed in a vacuum for 15 min to degas. Finally, the composite was cured at 80 °C for about 2 h in a heater. During the curing process, for alignment of NWs in PDMS matrix, the composite with the thickness of 1 mm has been subjected to a magnetic field. To confirm our NWs in alpha state, we use X-ray diffraction pattern. Our optical composite has been exposed to different hydrogen gas in our home-made chamber (Fig. 2). The sample was placed on a cylindrical prism by index matching gel in vacuum. Then, a sample was positioned into a gas chamber under the flow of dry nitrogen to remove any unwanted composition from its surface. Finally, the spectral response of the sample to different injections of H_2 gas has been recorded in our experimental setup as shown in Fig. 1.

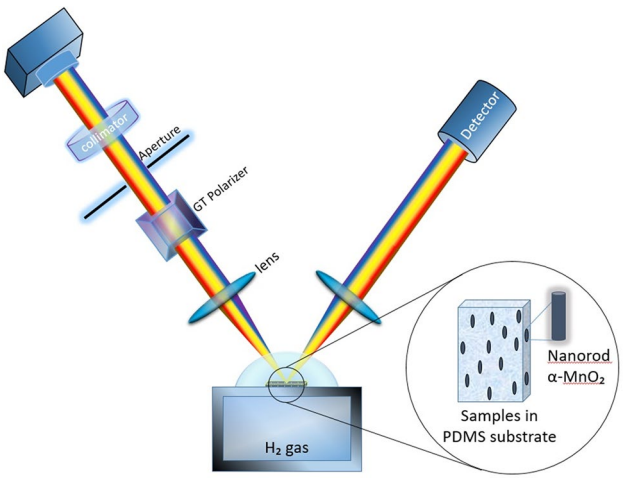

Fig. 1 Schematic diagram of the sensing experimental setup

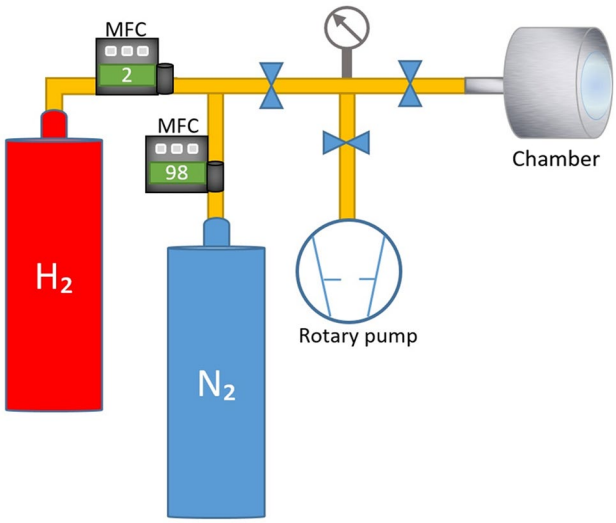

Fig. 2 Schematic diagram of the static gas volumetric method to fill gas in a chamber

The optical branch consisted of P- or S-polarized visible light which can be obtained by Glan–Taylor prism, sensor head and a spectrometer to record the response at various incident angles.

For hydrogen gas sensing confirmation, we use our ellipsometry quantity [19] as $\psi_{\text{eff}} = \frac{\psi_{H2} - \psi_{N2}}{\psi_{H2} + \psi_{N2}}$ in each gas concentration. In this parameter, ψ_{N2} and ψ_{H2} introduce ellipsometry parameter at pure N_2 and composition of H_2 and N_2 gas, respectively. In fact, to evaluate the sensing performances of the sample as H_2 gas sensor, we use the static volumetric method to fill our gas chamber by injecting known volumes of standard H_2 gas into a chamber equipped with N2 Gas by two mass flow controller (MFC) devices (Fig. 2).

For this step, the first MFC coupled to the H2 capsule was set to 2, 8 and 20 standard cubic centimeters per minute (SCCM) and the second ones were set to 400 SCCM for N_2 gas which these amounts yields to 0.5, 2 and 5% of H_2 gas in a chamber. In fact, we have 4800 part per million (ppm), 19,000 and 47,000 ppm for above mentioned H_2 percent, respectively (Fig. 3).

3 Results and discussions

The X-ray pattern of **α**-MnO_2 phase is presented in Fig. 4 which indicates the formation of the **α**-MnO_2 tetragonal phase [space group: I4/m (87)] that is according to JCPDS

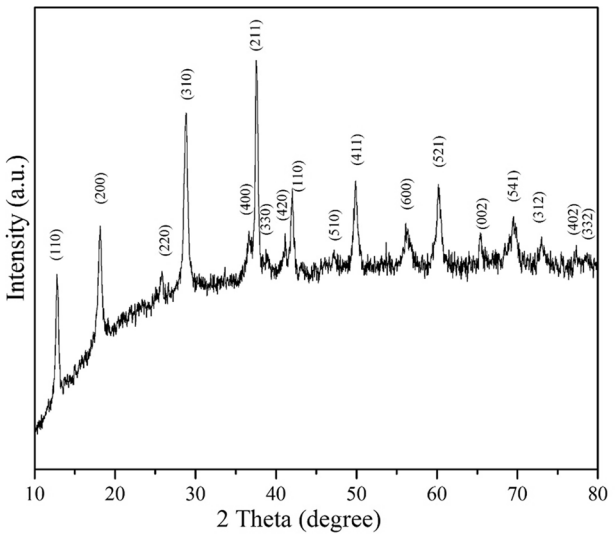

Fig. 3 The X-ray of α-MnO_2 prepared nanowires

data No. 44–0141 with no addition peaks of impurity. MnO_2 nanowires are well crystallized in the [211] lattice plane that has the most intensity. The average crystalline size was measured by Scherer formula:

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where $k = 0.9$ is factor shape, $\lambda = 1.5406$ Å, β is the full-width at half maximum in radian and θ is the angle on the maximum of the diffraction peak. Using the above formula, the average crystalline size was calculated to be 22 nm.

Figure 4 shows the image of as-prepared α-MnO_2 sample. The length and diameter of our nanowires are in the range of about 388–2055 nm and 25–58 nm, respectively, that is measured by image j software. (with about 50 numbers).

Afterward, our optical composite has been examined in different hydrogen gas concentration. For this purpose, we measured and calculated the optical ellipsometry parameters of the sample in each concentration of H_2 gas. At the first step, we measure the reflectance of the sample under N_2 gas and calculate ellipsometric parameters as shown in Fig. 5. In this measurement, the incidence angle of P- and S-polarized light was set to 20°.

At second step, the reflectance spectra of the sensor head was recorded with respect to different injections of H_2 gas (0.5, 2 and 5%) and the effective plasmonic ellipsometry as $\frac{\psi_{H2} - \psi_{N2}}{\psi_{H2} + \psi_{N2}}$. One can see the change in this effective parameter as a function of wavelength in different H_2 gas concentrations (Fig. 6a). The main peak of effective parameter has blue shift under different gas concentrations which confirms that the composite sample has a good sensitivity to different hydrogen gas concentrations in all of the visible regions (Fig. 6b).

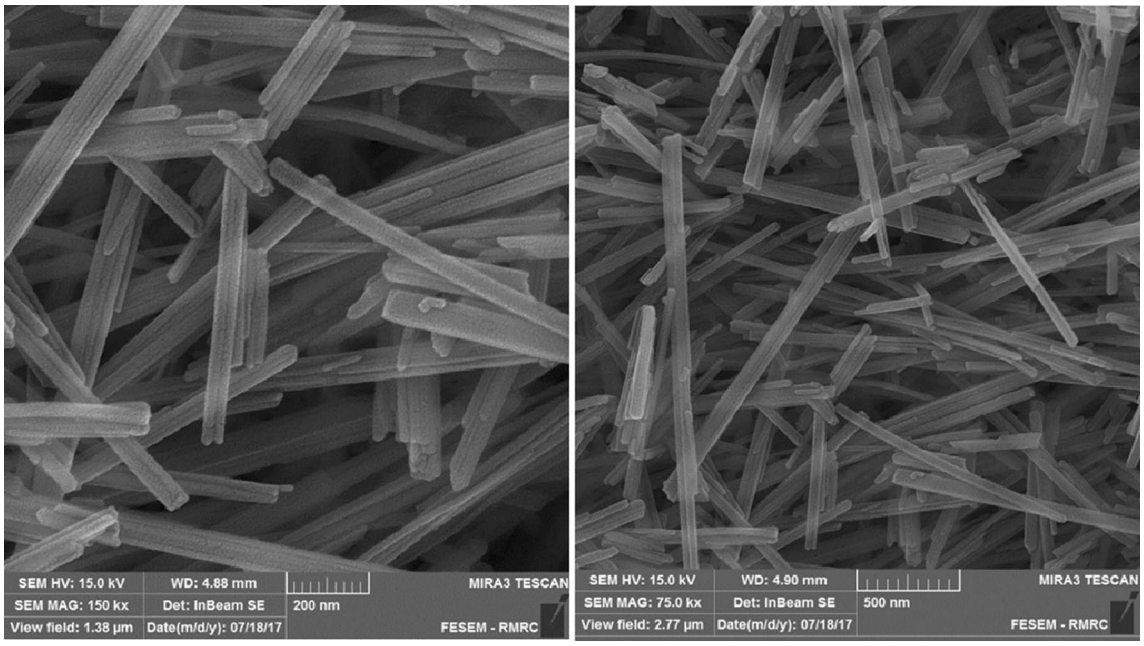

Fig. 4 SEM image of prepared α-MnO_2 nanowires with two different magnifications, 500 and 200 nanometer

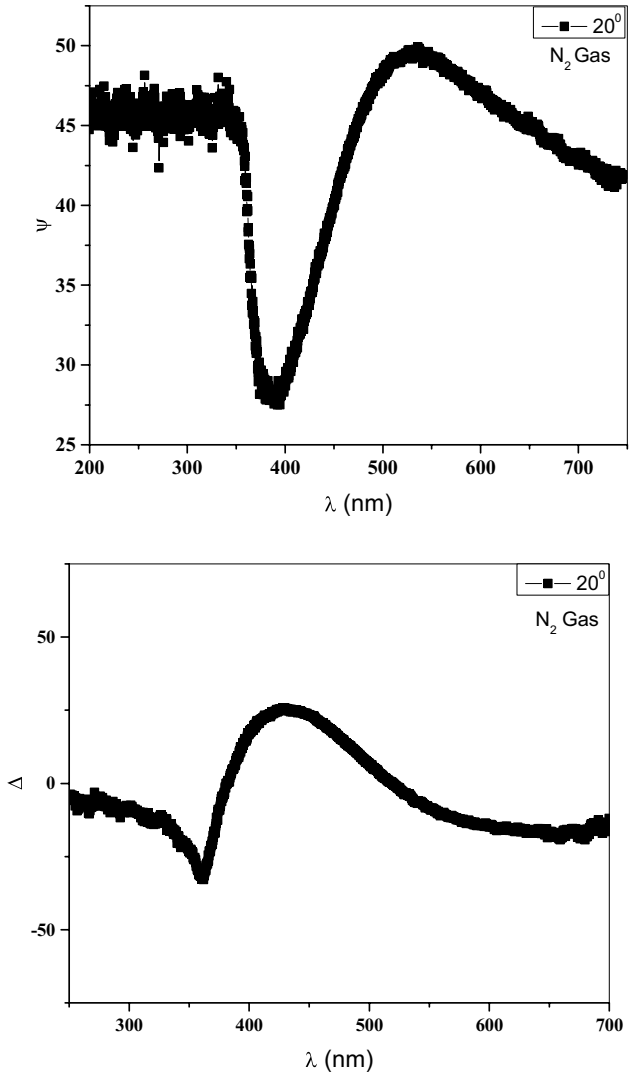

Fig. 5 Ellipsometric parameters of sample under pure N_2 gas at 20° incidence angle

In addition, we have efficient change in the effective ellipsometry parameter as a function of different gas concentrations as can be seen in Fig. 6c.

Thanks to the efficient crystalline nature of α-MnO_2 nanowires and also the high aspect ratio of them, we see sufficient sensitivity to the different hydrogen gas concentrations. In fact, due to much more free space between each nanowire and also above-mentioned high aspect ratio, we have two main reason for H_2 gas sensing. The first one is efficient site to absorb the gas between nanowires and the second one is the large surface to volume ratio of each nanowire.

Now based on the ellipsometric parameters such as the psi and delta, we can measure the change in the refractive indices of the samples under different gas concentrations. One may know that in PDMS matrix we have efficient oxygen concentrations as shown in Fig. 7.

For this reason, we have the potential of initial H_2O composition due to the exposure of the sample under H_2 gas purge and then produce the Mn(III)OO.H in the sample's surface. On the other word, we expect that the role of oxygen in the PDMs is the change of the surface composition from MnO_2 to Mn(III)OO·H with the effect of water oxidation (which is approved in MnO_2 materials [12]) and thus the change in the refractive index; the phase of the reflectance and, therefore, the ellipsometric parameters.

4 Conclusions

Overall, we have synthesized the high aspect ratio α-MnO_2 nanowires by the aid of hydrothermal effect and dispersed them into transmittive polymeric media to use them as an efficient hydrogen gas sensor. Our sample has been examined under different gas concentrations from 0 to 5% in vacuum chamber. The results indicate the logic change in the sample's response according to the different gas concentrations and one can see the linear behavior of resonance wavelength in ellipsometric parameter as a function of gas concentrations which indicate the sample's capability for hydrogen gas sensing practical applications.

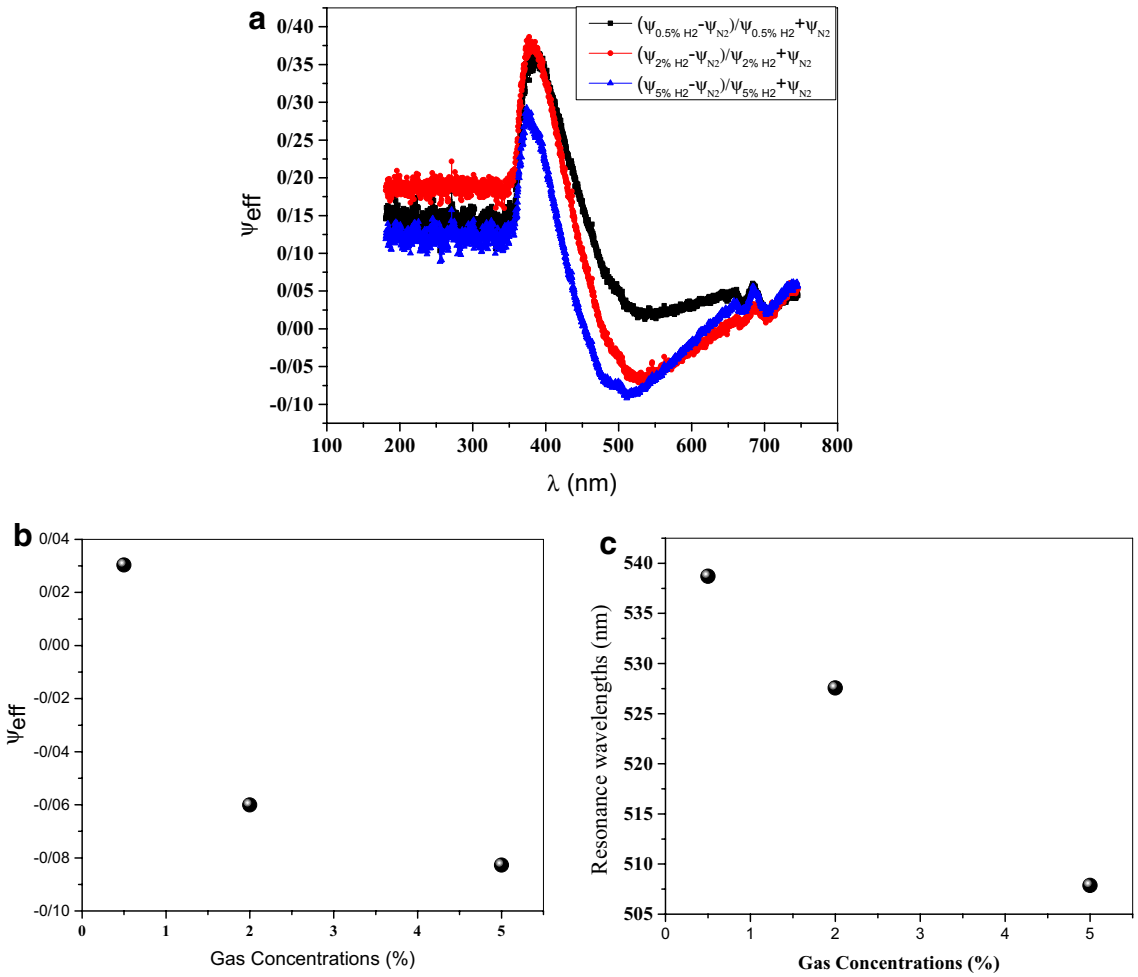

Fig. 6 **a** Ellipsometric effective parameter of the sample under different H_2 gas concentrations, **b** main peak of effective parameter and **c** resonance wavelength as a function of Gas concentartions

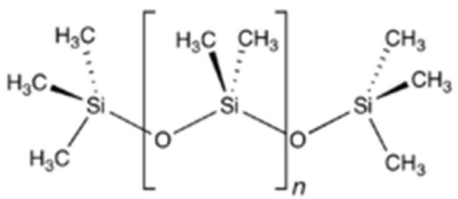

Fig. 7 The chemical structure of the ePDMS matrix

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