Rapid hydrogen sensing response and aging of $\alpha$-MoO$_3$ nanowires paper sensor

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**Abstract**

In order to improve the hydrogen sensing of transition metal oxide nanomaterials at room temperature, MoO$_3$ nanowire paper was prepared and used as a hydrogen sensing materials on substrate. In this paper, orthorhombic phase, ultra-long (~1 mm) MoO$_3$ nanowires were synthesized through conventional hydrothermal method at 260 °C for 96 h. A flexible nanowires paper with size of 200 mm x 300 mm was obtained by further self-assembly formation process of pure $\alpha$-MoO$_3$ nanowires in aqueous solution on hydrophobic substrate, and the thickness of paper can be controlled depend on the concentration of disperse nanowires. A novel hydrogen sensor with sensing area of 10 mm x 10 mm was obtained after Pt interdigital electrodes (IDE) deposited on the surface of $\alpha$-MoO$_3$ nanowires paper and transferred into ceramic circuit board (CCB) without any surface modification. The response and recovery time are about 3.0 and 2.7 s toward 1.5% H$_2$, respectively. The sensors also show good selectivity toward H$_2$ against other reduce gas, such as C$_2$H$_2$, CO and CH$_4$. Large amounts of the porous structures and high specific surface of nanowires paper is beneficial to the absorption of oxygen molecules, which would lead to the high sensitivity, fast response and recovery speed of sensor at room temperature. MoO$_3$ nanowires paper sensors have excellent stability and reliability, which could work for 5.56 years at room temperature.

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**Introduction**

For decades, hydrogen gas (H$_2$) is known as a clean, pollution-free and renewable energy and one of the most important gas carriers, which has been investigated in various ways to develop new alternative energy sources [1–3]. As a colorless and odorless flammable gas, H$_2$ has a number of unusual properties compare to other combustible gases, such as a very low density (0.0899 kg/m$^3$), a low minimum ignition energy (0.017 mJ), wide flammable range (4–75%) in the air [4,5]. However, H$_2$ leakage during production, storage, and...
transportation is a serious issue, which will lead to combustion even explosion as the concentration of \( \text{H}_2 \) reach up to 4% in the air. Therefore, it's significant to develop hydrogen sensor with reliable, fast response, good selectivity and long-term stability.

Up to now, several types of hydrogen sensors including optical fiber, electrochemical, metal oxide semiconductor (MOS) etc. have been developed [6–8]. Among them, hydrogen sensors based on MOS, such as \( \text{SnO}_2 \), \( \text{ZnO} \) and \( \text{TiO}_2 \) have been extensively studied and widely used in decades due to its low cost, flexibility, excellent stability and simple use in many fields [9–14]. It has been reported that the hydrogen responses of these materials are mainly related to the changes of carrier concentration or interface potential barrier. More specifically, under the condition of certain temperatures, an electron depletion layer can be formed near the surface of semiconductor materials due to the oxygen adsorption with the negative charge [15]. Heating is necessary for this type of hydrogen sensors, which still suffers from poor selectivity to other reducing gases. Therefore, in order to improve the \( \text{H}_2 \) sensing performance of MOS materials, individual \( \text{ZnO} \) nanowire due to its high specific surface area and full electron depletion, have been employed as sensing materials for building remarkable room temperature (RT) hydrogen sensors [16]. However, practical application is limit based on individual nanowire sensor thanks to its poor mechanical stability, a complex fabrication process, as well as a narrow detection range (it is prone to saturation for \( \text{H}_2 \)). Meanwhile, multiple nanowires can be assembled into arrays and networks to remediate the mechanical stability and detection range, while the RT response time of these array sensors is too long to be useful in practical applications. In recent year, Wang et al. reported the RT hydrogen sensing of \( \text{Nb}_2\text{O}_5 \) nanowires network, on which the response time is 1.67 min toward 2000 ppm \( \text{H}_2 \) [17]. Although the nanowire networks can improve the sensing properties under higher concentration of \( \text{H}_2 \), the response speed is still very slow due to the worse contact between nanowires.

Recently, some flexible nanowires paper structures, such as \( \text{MnO}_2 \), \( \text{V}_2\text{O}_5 \) etc., have been prepared through self-assembly formation process on hydrophobic substrate [18,19], which would improve the contact and electronic conductivity. Molybdenum trioxide (MoO\(_3\)) has two basic structures: the thermodynamically stable orthorhombic phase (\( \alpha \)-MoO\(_3\)), and the metastable monoclinic phase (\( \beta \)-MoO\(_3\)) [20,21]. The \( \alpha \)-MoO\(_3\) is an n-type wide band gap (3.2 eV) MOS, which possesses a unique double-layered structure in [010] direction, and with a large concentration of exposed active facets and exceptional electronic, optical and \( \text{H}_2 \) sensing properties [20]. In our previous work, \( \alpha \)-MoO\(_3\) nanoribbons membrane sensors exhibited high sensitivity to \( \text{H}_2 \) (as low as 500 ppb), good selectivity, and response time of 14.1 s toward 1000 ppm \( \text{H}_2 \) at room temperature [22]. In this work, ultra-long \( \alpha \)-MoO\(_3\) nanowires were synthesized by hydrothermal method at 260 °C, and a flexible \( \alpha \)-MoO\(_3\) nanowires paper with the size of 200 mm x 300 mm was obtained through self-assembly process on hydrophobic substrate. The detail schematic process is shown in Fig. 1. The sensors based on flexible \( \alpha \)-MoO\(_3\) nanowires paper exhibit excellent sensing performance towards \( \text{H}_2 \) with a concentration of 100 ppm to 1.5% which would be commercially available. In addition, the aging mechanism has also been discussed in detail.

**Experimental**

**Materials preparation and characterization**

Analytic grade \( \text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} \), \( \text{HNO}_3 \) and ethanol used in the experiment were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The \( \alpha \)-MoO\(_3\) nanowires paper was prepared on the following process. Firstly, the \( \alpha \)-MoO\(_3\) nanowires were synthesized via a hydrothermal method as reported in the literature [22]. The only difference is the hydrothermal temperature (230–260 °C). Specifically, 0.01 mol \( \text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} \) was dissolved into 32.75 ml deionized (DI) water and the mixture was continuously stirring for 30 min to obtain homogeneous solution. Then 7.25 ml of concentrated \( \text{HNO}_3 \) was added into the above solution and stirring for 10 min. The final precursor was transferred into a Teflon-lined 50 ml stainless steel autoclave and sealed for hydrothermal treatment at 230–260 °C for 96 h. After the autoclave was cooled down naturally to room temperature (RT), \( \alpha \)-MoO\(_3\) nanowires were obtained. Secondly, the as-synthesized nanowires were transferred into a 2 L glass vessel with 1.5 L DI water and ethanol mixture. Then a stable wool-like suspension was formed by vigorously stirring the mixture for 24 h. Then the suspension was transferred into a Teflon container with the size of 200 mm x 300 mm x 40 mm for self-assembly for 24 h. After removed the upper solution in the

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Fig. 1 – The schematic process of the preparation of hydrogen sensor. (I) The synthesis of ultra-long length \( \alpha \)-MoO\(_3\) nanowires by hydrothermal method. (II) The self-assembly process of nanowires on Teflon container. (III) The \( \alpha \)-MoO\(_3\) nanowires paper is obtained after drying and pressing. (IV) The hydrogen sensor is produced after cutting, deposition of Pt interdigital electrode and intergraded on ceramic circuit board (CCB).

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container, a membrane was formed and followed by dried at 50 °C for 12 h. Finally, a white free-standing nanowires paper was obtained which can be teared off directly from the Teflon, as shown in Fig. 1 (step I to III). The thickness of the paper can varied from several to hundred micrometers depends on the concentration of the suspension deposited on the substrates. The phase structure of the samples were determined by X-ray diffraction (XRD, Bruker D8A25, CuK, λ = 1.5406 Å). The morphology and the microstructure were characterized by field-emission scanning electron microscope (FESEM, JEOL JSM 7100F) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM 2010).

The fabrication and testing of hydrogen sensor

The obtained α-MoO3 nanowires paper was mechanized isostatic pressing and cut into a small piece of paper with uniform size (10 mm × 10 mm), and following Pt interdigital electrodes were deposited on the surface of paper by DC magnetron sputtering process, the spacing between two adjacent electrodes was 50 μm. Then hydrogen sensors were produced after integrated the small piece of paper into ceramic circuit board (CCB) and bonded by copper wire (step IV in Fig. 1). Room temperature H2 sensing properties were tested by monitoring the resistance changes of the sensors in a homemade testing system. The gas concentration was controlled by the gas flow-through method. The initial resistance was indicated the resistance of the device in the air and controlled by the gas flow-through method. The initial resistance was controlled by the gas flow-through method. The initial resistance was indicated the resistance of the device in the air and controlled by the gas flow-through method. 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Results and discussions

To determine the influence of hydrothermal temperature on the phase structure of the obtained samples, XRD patterns of MoO3 nanowires obtained at four different temperatures (230, 240, 250 and 260 °C) are shown in Fig. 2. As can be seen that all the synthesized samples were indexed to the orthorhombic phase MoO3 (α-MoO3) (JCPDS Card No. 05-0508). From the diffraction peaks of (020), (040), and (060), it’s obvious that MoO3 nanowires grew along (060) preferred orientation (similar results can also be found in the recent literature [23]). As the temperature increased, the intensities of diffraction peaks increased and diffraction angle (2θ) shifted to higher angle (as shown in the inset in Fig. 2b), which indicated the temperature has a significant impact on the crystallinity and interplanar spacing of nanowires. The relationship between d006 spacing and hydrothermal temperature were calculated according to the Bragg’s law, as shown in Fig. 2b. We can see that d006 spacing is about 4.6368 Å for MoO3 nanowires synthesized at 230 °C, which is almost unchanged for MoO3 nanowires obtained at 240 °C. As the temperature increased from 240 to 260 °C, the d006 spacing reduced from 4.6368 to 4.607 Å (the change rate is about 0.64%), indicating MoO3 nanowires obtained at higher temperature have larger inner stress. It has been reported that the stoichiometry have changed with increasing hydrothermal temperature [22], suggesting the increase of the amount of Mo5+- and a strong correlation between the surface adsorption of oxygen species and Mo5+- content, which could lead to the increasing of inner stress within the lattice of MoO3 nanowire. Hence, MoO3 nanowires obtained at 260 °C were selected as the sample for further assembly on hydrophobic substrate.

In order to reveal the microstructural properties and assembled morphologies of α-MoO3, the SEM and TEM images of MoO3 nanowires obtained at 260 °C and the digital photos of the corresponding self-assembly nanowire paper are shown in Fig. 3. As shown in Fig. 3a–d, the as-synthesized α-MoO3 nanowires have good dispersion, uniform diameter (~300 nm), long length (~1 mm) and high crystallinity (single crystal). A typical sample of the self-assembly nanowire paper is shown in Fig. 3d. One can see that large scale nanowires membrane with uniform surface morphology and the size of 200 mm × 300 mm were achieved within Teflon container, which also exhibits an extremely flexibility and extensibility with twisting and folding for over 10 times, as shown in the inset in Fig. 3d and Supporting Information (Fig. S2). Fig. 3e–g

![Fig. 2](image-url) – (a) XRD patterns of the MoO3 nanowires obtained by hydrothermal method at four different temperatures (from 230 to 260 °C), (b) The relationship between interplanar spacing of (060) planes and hydrothermal temperature.
shows the SEM images of cross-section and surface of α-MoO₃ nanowire paper. It’s obvious that the obtained α-MoO₃ nanowire paper has the uniform thickness of about 100 μm, which was formed by nanowire layers connected randomly and stick together tightly. Specially, the surface of the self-assembly paper-like networks followed one direction under nature conditions, and the nanowires paper has many porous between the layers, which should be beneficial to the rapid response of the gas sensor.

To investigate the hydrogen gas sensing performance at room temperature (RT), the α-MoO₃ nanowire paper with size of 10 mm × 10 mm were directly fixed on a homemade test system, and 5.0 V DC voltage was applied to keep the resistance stable for several hours. Fig. 4a shows the comparison of hydrogen gas sensing performance of α-MoO₃ nanowires paper obtained at four different temperatures (the inset is the prototype of hydrogen sensor). It’s obvious that α-MoO₃ nanowires synthesized at different temperatures have various hydrogen sensing performances. The sensitivity factor (S) is defined as $S = \frac{\Delta R}{R_{\text{air}}} = \frac{R_{\text{air}} - R_{\text{gas}}}{R_{\text{air}}}$, where $\Delta R$ is the difference between the resistance in air ($R_{\text{air}}$) and in target gas ($R_{\text{gas}}$) [17]. The response time ($t_{\text{res}}$) and recovery time ($t_{\text{rec}}$) are defined as the time required for the sensor to reach 90% of the final response and recovery. As the temperature increased from 230 °C to 260 °C, the normalized sensitivity factor toward 1.5% H₂ is enhanced from 0.7 to 0.85. The response time ($t_{\text{res}}$) and the recovery time ($t_{\text{rec}}$) are 3.0 s and 2.7 s for α-MoO₃ nanowires paper obtained at 260 °C (as shown in Fig. 4b), significantly faster than α-MoO₃ nanoribbons membrane sensors [22], which can meet the alarm time of the practical requirements for the hydrogen leakage (the national standard response time limit is 30 s).

Fig. 4c shows the response repeatability of α-MoO₃ nanowires paper sensor toward 1.5% H₂. We can see that the sensitivity, response time and recovery time are nearly unchanged after many cycled testing (seven cycles were offered here), indicating the excellent repeatability of α-MoO₃ nanowires paper sensor. In addition, the sensors are also sensitive to H₂ with the concentration below 1.5%, as shown in Fig. 4d. As the concentration of H₂ decreased, the response time is increased. Specifically, for 1.2% H₂, the response time is 6 s and recovery time is 11 s, which will reach up to 28 s and 42 s for 500 ppm H₂, respectively.

To test the selectivity of α-MoO₃ nanowire paper sensor towards H₂, several potential interferential reducing gases including ethanol vapor (C₂H₅OH), carbon monoxide (CO), and methane (CH₄) were investigated, and the concentrations are 2000 ppm, as shown in Fig. 5. The sensitivity factors toward C₂H₅OH ($\beta = 0.2$), CO ($\beta = 0.01$) and CH₄ ($\beta = 0.01$) are much lower than that of H₂ ($\beta = 0.9$), indicating a remarkably high selectivity of α-MoO₃ nanowire paper sensor toward H₂. As mentioned above, there is a strong correlation between Mo⁵⁺ content and the surface adsorbed oxygen, i.e., MoO₃ nanowires with more Mo⁵⁺ content have more adsorbed oxygen on the surface of nanowires. As the target gases contact with MoO₃ nanowires, which would prefer to react with adsorbed oxygen on the surface of nanowires. Therefore, the sensing performance of our sensors to all the target gases could be attributed to the redox reaction with the adsorbed oxygen molecules. In addition, the redox reaction itself between H₂...
and absorption oxygen species is selective, which is more easily generate proton H under the catalysis of adsorbed oxygen than other gas, such as C2H5OH, CO and CH4. As a result, α-MoO3 nanowire paper sensor shows a higher response to H2 against C2H5OH, CO and CH4.

As for the MOS hydrogen sensor, stability and reliability are also important factors besides the high sensitivity, good repeatability and selectivity [24]. To investigate the stability and reliability, the nanowires paper sensors were put into the aging test chamber (relative humidity of 95%, relative temperature of 70 °C) and monitored for 80 day period, where on each four days the sensor was exposed to H2 gas at a 1.5% concentration. Fig. 6a shows the time dependence of sensor response monitored for 80 day period. It is obvious that the sensitivity of sensor was almost unchanged with the extension of testing time, which indicates the sensor is quite stable and its gas sensing property is almost not influenced by the atmosphere during the aging process. Fig. 6b shows the comparison of XRD patterns of the MoO3 nanowires paper before and after aging testing. As shown, the diffraction peaks of nanowire paper were split after aging for 40 days, and the split level was enhanced for the sample aging for 80 days, revealing a phase transformation occurred after the aging testing. This new phase could relate to the metastable phase of MoO3 (β-MoO3), which will change back α-MoO3 easily as the sensor was exposed to the H2 gas environment.

It’s been reported that acceleration factor (AF) is used to derate the failure rate from the thermally accelerated life test conditions to a failure rate indicative of actual use temperature [25,26]. According to the Arrhenius equation, the acceleration factor can be obtained as followed [20]:

$$AF = \frac{L_{\text{use}}}{L_{\text{stress}}} = \exp \left[ \frac{E_a}{k} \left( \frac{1}{T_{\text{use}}} - \frac{1}{T_{\text{stress}}} \right) \right]$$

where $E_a$ is the thermal activation energy, $k$ is the Boltzmann’s constant (8.63 × 10^-5 eV/K), $T_{\text{use}}$ is the normal use temperature of the sensor, $T_{\text{stress}}$ is the life test stress temperature, $L_{\text{use}}$ is the normal lifetime (days) of the sensor, and $L_{\text{stress}}$ is the lifetime (days) on the stress condition. For oxide defects failure mechanism, activation energy is 0.3–0.5 eV [25]. The actual use temperature of the sensor is 293 K, and the stress temperature is 343 K. Considering that the activation energy of the sensor is 0.35 eV, and its failure of the sensitivity controlled by within 5%. Actually, the sensor is failure after aging for 360 days ($L_{\text{stress}} = 360$) through the fitting results of sensitivity. Therefore, the normal lifetime ($L_{\text{use}}$) of the sensor based on α-MoO3 nanowire paper is about 2030 days (~5.56 years).

Fig. 4 – The gas sensing performance of the flexible MoO3 nanowires paper sensor. (a) The sensitivities of different sensors (MoO3 nanowires obtained by different hydrothermal temperatures) toward 1.5% H2. (b) The first cycle to 1.5% H2. (c) Repeatability to 1.5% H2. (d) Dynamic response resistances of the flexible nanowires paper for different H2 concentration (100 ppm–1.5%).

Fig. 5 – The selectivity of MoO3 nanowires paper sensor tested by various gases (2000 ppm of H2, C2H5OH, CO and CH4, respectively).
according to the calculation result of Arrhenius equation, which means MoO₃ nanowires paper sensors have excellent reliability.

**Conclusions**

α-MoO₃ nanowire paper with the size of 200 mm × 300 mm were fabricated by self-assembly of ultra-long α-MoO₃ nanowires on hydrophobic substrate. The nanowires paper sensor has excellent hydrogen sensing response toward 100 ppm to 1.5% H₂ concentration at room temperature, which could attribute to the porous structures and high specific surface of nanowires paper. As for 1.5% H₂ concentration, the response and recovery time are about 3.0 s and 2.7 s, respectively. The response speed will reduce as the H₂ concentration decreased. The sensors also show good selectivity toward H₂ against other reduce gas, such as C₂H₅OH, CO and CH₄. In addition, MoO₃ nanowires paper sensors have excellent stability and reliability, which could work for 5.56 years at room temperature. The fabrication process of hydrogen sensor based on α-MoO₃ nanowires paper offered in this work will commercially available in the future.

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**Appendix A. Supplementary data**

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2017.01.116.

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**REFERENCES**


