

Colorimetric Sensor Based on Pd–MoO₃ Nanowires for Hydrogen Gas Leak Detection

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Abstract

The early detection of hydrogen gas leaks is crucial because of their high explosion risk. Current oxide–semiconductor-based hydrogen sensors are reliant on electrical circuits that may fail during accidents and require high temperatures, thereby raising safety concerns. Thus, there is an urgent need for the development of simpler and more intuitive sensors that can operate at room temperature. This study proposed a hydrogen sensor based on Pd–MoO₃ nanowires. The sensor exhibited a visible color change upon exposure to hydrogen at room temperature. The Pd–MoO₃ nanowires were synthesized by decorating the surface of hydrothermally produced MoO₃ nanowires with 1–5 wt.% Pd. Upon exposure to 5% hydrogen gas at room temperature, all Pd–MoO₃ nanowires exhibited distinct color changes (ΔE). In particular, the MoO₃ nanowires with 3 wt.% Pd (3Pd–MoO₃) yielded an exceptionally high ΔE value of over 15 within 10 min. Further, the 3Pd–MoO₃ nanowires exhibited a noticeable color change ($\Delta E > 1.6$) within 2 min, demonstrating their potential for highly sensitive and rapid hydrogen detection. The outstanding color change of the 3Pd–MoO₃ nanowires was attributed to valence changes in both Mo (Mo⁶⁺ and Mo⁵⁺) and Pd (Pd²⁺ and Pd⁰) upon exposure to hydrogen.

Keywords: Colorimetric sensor, Hydrogen detection, Pd–MoO₃, Nanowires, Hydrothermal synthesis

1. INTRODUCTION

Hydrogen energy is increasingly being recognized as a viable alternative to fossil fuels, with widespread applications in industries such as petrochemicals, semiconductors, refining, and fuel cells [1]. Recently, they have gained attention as a power source for mobility and power generation because of their high energy density (120 MJ/kg) [2]. However, hydrogen poses a significant explosion risk when its concentration in air exceeds 4% [3]. Moreover, its flames are extremely difficult to extinguish once ignited [4]. Therefore, careful monitoring of hydrogen gas leakage is crucial. Because hydrogen is a colorless and odorless gas that cannot be detected by humans, a detector is essential for identifying leaks.

Current hydrogen detectors such as gas chromatography-flame ionization detectors offer precise detection at low concentrations

[5]. However, these detectors are bulky, expensive, and time consuming, thereby rendering them unsuitable for real-time monitoring. Oxide semiconductor gas sensors such as those made using SnO₂, In₂O₃, and WO₃ provide a compact and cost-effective alternative for real-time detection [6,7]. Nevertheless, their reliance on electric circuits and high operating temperatures (*e.g.*, 200–400°C) serve as bottlenecks. Thus, there is need to develop new sensors capable of rapid and intuitive detection of hydrogen at room temperature.

Colorimetric gas sensors, which change color upon the interaction of their sensing materials with specific gases, can detect hydrogen without requiring complex electrical devices [8]. In addition, these sensors are safe because their room-temperature operability reduces the ignition risk. These advantages render colorimetric gas sensors viable candidates for early hydrogen leak detection.

Among the various colorimetric materials, MoO₃ is particularly promising for hydrogen detection because of its ability to change color upon exposure to hydrogen [9]. For instance, Sun et al. [10] reported that MoO₃ nanobelts changed color from light gray to dark blue in the presence of hydrogen. Pd is another favorable material for colorimetric hydrogen sensing because of its ability to change color in the presence of hydrogen [11]. The excellent colorimetric properties of MoO₃ and Pd suggest that their combination can facilitate the development of highly effective

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(Received: Aug. 23, 2024, Revised: Sep. 2, 2024, Accepted: Sep. 9, 2024)

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colorimetric hydrogen sensors.

This study investigated the colorimetric hydrogen-sensing properties of Pd–MoO₃ nanowires. Pd–MoO₃ nanowires were prepared by decorating the surface of hydrothermally synthesized MoO₃ nanowires with 1–5 wt.% Pd. Subsequently, a hydrogen sensor was fabricated by screen printing the nanowires onto a glass slide. All Pd–MoO₃ sensors demonstrated colorimetric hydrogen-sensing properties at room temperature. Among the sensors, those containing 3 wt.% Pd exhibited a drastic color change from light brown to dark gray, which is not typical of MoO₃ or Pd alone under hydrogen exposure. Therefore, the color-change mechanism is discussed. This study aimed to demonstrate the potential of Pd–MoO₃ for visible hydrogen detection and elucidate its colorimetric hydrogen-sensing mechanism.

2. EXPERIMENTAL

2.1 Synthesis of Pd–MoO₃ nanowires

MoO₃ nanowires were synthesized by dissolving 0.01 mol of Na₂MoO₄·2H₂O (≥99.5%, Sigma-Aldrich, USA) and 7.25 ml of HNO₃ (ACS reagent 70%, Sigma-Aldrich, USA) in 32.75 ml of distilled water. Subsequently, this solution was in an autoclave and subjected to hydrothermal treatment at 200°C for 12 h. To synthesize Pd–MoO₃ nanowires, 0.2 g of MoO₃ nanowires were dispersed in H₂PdCl₄ solutions of varying concentrations. A H₂PdCl₄ solution was prepared by dissolving PdCl₂ (99%, Sigma-Aldrich, USA) in HCl (ACS reagent 35%, Sigma-Aldrich, USA) in a 1: 2 ratio. In particular, 0.2, 0.6, and 1.0 mg of PdCl₂ were used at HCl concentrations of 0.2, 0.7, and 1.2 μL to achieve different Pd concentrations. The mixture was stirred for 30 min to ensure uniform Pd distribution on the MoO₃ nanowire surface. Thereafter, the mixture was centrifuged five times with ethanol and distilled water, followed by drying at 40°C for 6 h to obtain Pd–MoO₃ nanowires. For simplicity, the MoO₃ nanowires decorated with 1, 3, and 5 wt.% Pd are referred to as 1Pd–MoO₃, 3Pd–MoO₃, and 5Pd–MoO₃, respectively.

2.2 Fabrication of Pd–MoO₃ colorimetric sensor

The colorimetric sensor was fabricated by mixing 0.03 g of Pd–MoO₃ nanowires with 50 μL of a binder (α -terpineol, 90% technical grade, Sigma-Aldrich, USA) to form a slurry. This slurry was then screen-printed onto a glass slide (area = 10 mm × 30 mm) and then dried in an oven at 70°C for 2 h.

2.3 Characterization

The crystal structures of the Pd–MoO₃ nanowires were analyzed by X-ray diffraction (XRD, SmartLab, Rigaku, Japan). The compositions and chemical states of the nanowires were confirmed via X-ray photoelectron spectroscopy (XPS, Sigma Probe, Thermo VG Scientific). The morphology and microstructure of the nanowires were observed through field-emission scanning electron microscopy (FE-SEM; S-4700, Hitachi, Japan) and spherical aberration-corrected transmission electron microscopy (TEM; JEM-ARM200F, JEOL, Japan).

2.4 Hydrogen sensing test

The colorimetric properties of the sensors in response to hydrogen were evaluated in a quartz chamber connected to a gas-supply system. The chamber atmosphere was controlled by flowing dry air (99.999%, Hankook Special Gases) and hydrogen gas (5%, Hankook Special Gases) using mass flow controllers (MFC) in the gas supply system. The flow rate was fixed at 500 cm³·min⁻¹, and all measurements were conducted at room temperature (17±3°C). The color change of the sensor was monitored in real time using a smartphone camera. The intensity of the color change was quantified based on calculations of the color difference (ΔE) between two colors within the International Commission on Illumination (CIE) L^{*}a^{*}b^{*} color space [12], using the following equation:

$$\Delta E = \sqrt{(L - L')^2 + (a - a')^2 + (b - b')^2} \quad (1)$$

where L, a, and b are the lightness, red-green position, and yellow-blue position of the sample, respectively.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of Pd–MoO₃ nanowires

XRD analysis was performed to confirm the phases of the MoO₃ and Pd–MoO₃ nanowires (Fig. 1). All samples exhibited the orthorhombic phase of MoO₃ (α -MoO₃) (JCPDS #05-0508). The diffraction peaks were predominantly oriented along the (020), (040), and (060) directions, suggesting that the MoO₃ crystals grew mainly along the b-axis during the hydrothermal process. Further, no Pd-related peaks were observed in any of the Pd–MoO₃ samples, which may be because of the low concentration of Pd.

Fig. 2 (a–d) show SEM images of the MoO₃ and Pd–MoO₃

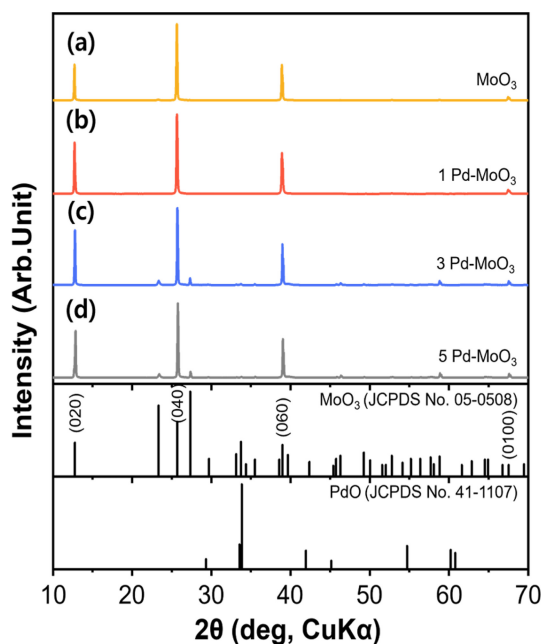


Fig. 1. XRD patterns of (a) MoO₃, (b) 1Pd–MoO₃, (c) 3Pd–MoO₃, and (d) 5Pd–MoO₃ nanowires

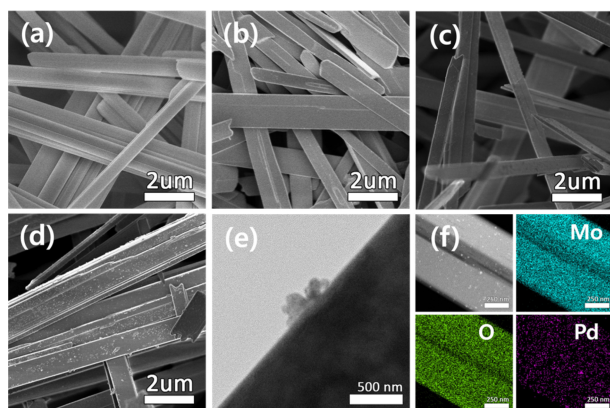


Fig. 2. SEM images of (a) MoO₃, (b) 1Pd–MoO₃, (c) 3Pd–MoO₃, and (d) 5Pd–MoO₃ nanowires. (e) TEM image of 3Pd–MoO₃. (f) Elemental mapping of 3Pd–MoO₃.

nanowires. The MoO₃ nanowires had a diameter of approximately 0.5 μm and lengths ranging as 10–20 μm (Fig. 2 (a)). The Pd decoration did not significantly alter the overall wire-like morphology, although it might have slightly affected the surface texture and uniformity of the wires (Fig. 2 (b–d)). Both the SEM and TEM images confirmed the anisotropic growth of the nanowires, which was consistent with the XRD results.

Fig. 2 (e) shows a TEM image of the 3Pd–MoO₃ nanowires. As evident, Pd was decorated on the surface of the MoO₃ nanowires in the form of nanoparticles. The TEM elemental mapping of 3Pd–MoO₃ (Fig. 2 (f)) demonstrated a uniform distribution of Pd nanoparticles (size = approximately 100 nm).

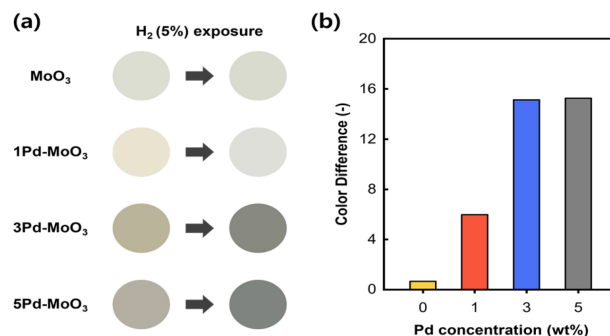


Fig. 3. (a) Photographs of the MoO₃ and Pd–MoO₃ sensors before (left) and after 10 min of exposure to 5% hydrogen (right). (b) Color differences (ΔE) of the MoO₃ and Pd–MoO₃ sensors after 10 min of exposure to 5% hydrogen.

3.2 Hydrogen sensing properties of Pd–MoO₃ nanowire-based colorimetric sensors

Fig. 3 illustrates the colorimetric responses of the MoO₃ and Pd–MoO₃ sensors to hydrogen. The sensors were exposed to 5% hydrogen for 10 min and their real-time color changes were monitored via a smartphone camera.

Fig. 3 (a) shows the color changes of the sensors after 10 min of exposure to 5% hydrogen. The pure MoO₃ sensor demonstrated negligible color change; however, the Pd–MoO₃ sensors exhibited significant color shifts. Specifically, all the Pd–MoO₃ sensors initially had brownish colors that gradually shifted to grayish colors. These results indicate a particularly active surface reaction between Pd–MoO₃ and hydrogen.

Fig. 3 (b) shows the color difference observed in the Pd–MoO₃ sensors following exposure to 5% hydrogen. The ΔE values for the 1Pd–MoO₃, 3Pd–MoO₃, and 5Pd–MoO₃ sensors were 6.00, 15.1, and 15.3, respectively. Thus, the color change plateaued when the Pd content exceeded 3 wt.%. Therefore, decorating 3 wt.% Pd is cost-effective for the detection of hydrogen with a maximum ΔE .

To evaluate the hydrogen detection speed of the 3Pd–MoO₃ sensor, the color change was monitored at different hydrogen exposure times. The initial color of the 3Pd–MoO₃ sensor was light tan (#BAB49B), which transitioned to dark gray (#888981) following exposure to 5% hydrogen for 10 min (Fig. 4 (a)). Fig. 4 (b) illustrates the progression of the color change over time. Images were captured at 2, 5, 7, and 10 min. The corresponding ΔE values were 9.04, 11.9, 13.4, and 15.1, respectively. As evident, the sensor began to exhibit a distinguishable color change ($\Delta E > 1.6$ [13]) within 2 min. This rapid response underscores the potential of the 3Pd–MoO₃ sensor for early detection of hydrogen gas leaks.

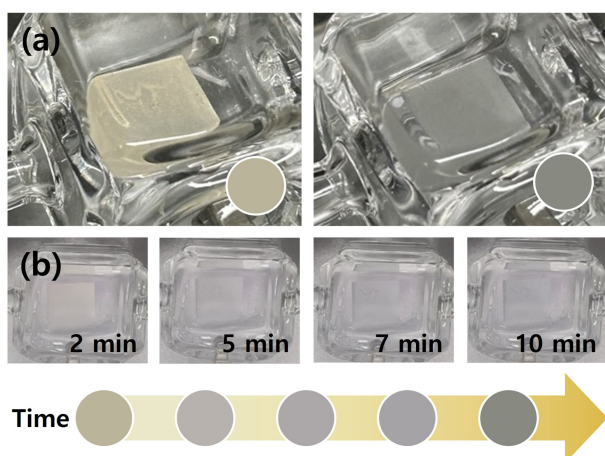


Fig. 4. (a) Photographs of 3Pd–MoO₃ sensor before (left) and after 10 min of exposure to 5% hydrogen (right). (b) Photographs of the 3Pd–MoO₃ sensor during color change (exposure to 5% H₂) at intervals of 2–3 min.

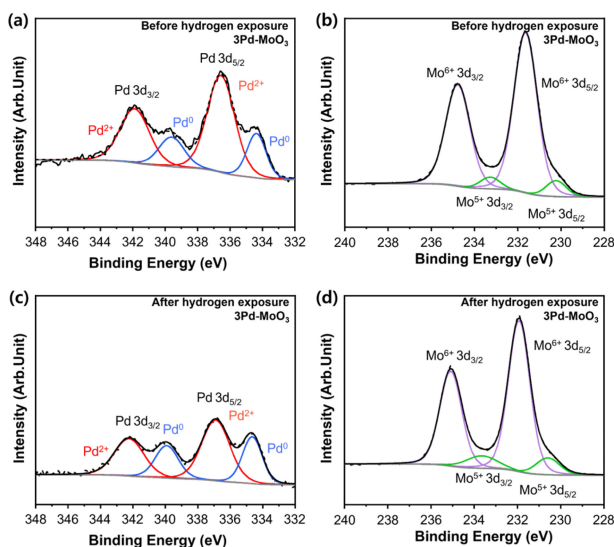


Fig. 5. (a) XPS Pd 3d spectrum and (b) Mo 3d spectrum of the 3Pd–MoO₃ before hydrogen exposure. (c) XPS Pd 3d spectrum and (d) Mo 3d spectrum of the 3Pd–MoO₃ after 10 min of exposure to 5% hydrogen.

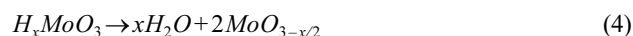
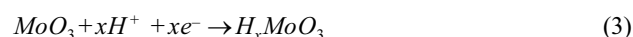
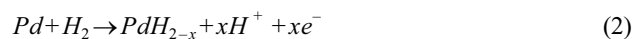
3.3 Colorimetric mechanism of Pd–MoO₃ nanowires upon exposure to hydrogen

To understand the colorimetric hydrogen sensing mechanism of the 3Pd–MoO₃ nanowires, XPS analysis was conducted before and after exposure to 5% hydrogen (Fig. 5). The Pd 3d XPS spectrum before hydrogen exposure revealed the presence of both Pd²⁺ and Pd⁰ peaks (Fig. 5 (a)). This indicated the partial oxidation of Pd to PdO during the synthesis process. Pd²⁺ peaks typically appeared at 337.4 and 342.6 eV [14] at higher binding energies

compared to the Pd⁰ peaks (335.0 and 340.3 eV) [15]. In the Mo 3d XPS spectrum prior to hydrogen exposure, the peaks corresponding to Mo⁶⁺ were observed at 232.9 and 236.0 eV, along with smaller peaks for Mo⁵⁺ at 231.7 and 234.8 eV [10] (Fig. 5 (b)). This indicated the multivalent (Mo⁵⁺/Mo⁶⁺) nature of MoO₃.

After 10 min of exposure to 5% hydrogen, the Pd and Mo 3d XPS spectra exhibited significant changes. The Pd 3d spectrum (Fig. 5 (c)) revealed an increase in the Pd⁰ peak intensity and decrease in the Pd²⁺ peaks. This implied the reduction of PdO by hydrogen. Similarly, the Mo 3d spectrum (Fig. 5 (d)) exhibited an increase in the Mo⁵⁺ peaks, implying that MoO₃ was also reduced by hydrogen. The results of the quantitative analyses are presented in Table 1.

Based on XPS analysis, the colorimetric hydrogen sensing mechanism can be explained as follows [10]:



Upon the exposure of Pd–MoO₃ to hydrogen, hydrogen molecules first adsorbed onto the Pd surface and dissociated into protons (H⁺) and electrons (e⁻) (Eq. 2). These protons and electrons were then transferred to the MoO₃ surface via a spillover mechanism [16]. Subsequently, the H⁺ ions diffused into the MoO₃, primarily interacting with the oxygen to form H_xMoO₃ (Eq. 3). Simultaneously, certain OH₂ groups on the H_xMoO₃ surface detached as water molecules, thereby facilitating the formation of sub-stoichiometric MoO_{3-x/2} (Eq. 4). This process reduced Mo⁶⁺ to Mo⁵⁺, which corresponded to the changes observed in the Mo 3d XPS spectra (Fig. 5 (b), (d)).

During this process, the energy bandgap of MoO₃ narrowed, resulting in a color change in the material. Pristine MoO₃ is a semiconducting material (a band gap of 3.2 eV), wherein Mo⁶⁺ and O²⁻ form the conduction and valence band states, respectively. The generation of Mo⁵⁺ creates new energy states within the bandgap, effectively narrowing it and causing a color change. Borgschulte et al. [17] reported that MoO_{3-x/2} appears blue because of intervalent charge transfer from Mo⁵⁺ to Mo⁶⁺ upon optical excitation.

However, the 3Pd–MoO₃ in this study turned dark gray in hydrogen atmosphere. This suggested the influence of additional factors. This change was attributed to the colorimetric response of PdO. When exposed to hydrogen, PdO changes color owing to its

Table 1. Relative fraction of Pd²⁺, Pd⁰, Mo⁶⁺, and Mo⁵⁺ in the XPS Pd and Mo 3d spectra of the 3Pd–MoO₃ before and after 10 min of exposure to 5% hydrogen.

Samples	Pd ⁰ , Pd 3d _{5/2}	Pd ⁰ , Pd 3d _{3/2}	Pd ²⁺ , Pd 3d _{5/2}	Pd ²⁺ , Pd 3d _{3/2}
Pd–MoO ₃	13.64	11.72	43.98	30.67
Pd–MoO ₃ After H ₂	20.63	16.65	38.08	24.64
Samples	Mo ⁶⁺ , Mo 3d _{5/2}	Mo ⁶⁺ , Mo 3d _{3/2}	Mo ⁵⁺ , Mo 3d _{5/2}	Mo ⁵⁺ , Mo 3d _{3/2}
Pd–MoO ₃	35.56	55.17	4.79	3.49
Pd–MoO ₃ After H ₂	34.11	53.06	6.51	6.33

reduction to Pd as per the following equation (Eq. 5). It appears dark brown at the nanoscale (100–200 nm) [18,19].



Notably, blue and dark brown are complementary colors; therefore, when combined, they produce a color similar to black, such as dark gray. Considering the significant PdO-to-Pd reduction observed in the XPS analysis (Fig. 5 (a), (c)), the dark gray color change resulting in the high ΔE may be attributable to the combined effects of the color shifts in both MoO₃ and Pd. This finding highlights the manner in which the colorimetric properties of a material can be enhanced through the synergistic effects of the reduction of its components.

4. CONCLUSIONS

This study investigated the colorimetric hydrogen-sensing properties of MoO₃ nanowires decorated with 1–5 wt.% Pd. All Pd–MoO₃ nanowires exhibited a visible color change when exposed to 5% hydrogen. In particular, the MoO₃ nanowires with 3 wt.% Pd (3Pd–MoO₃) exhibited significant color change, with an ΔE value that exceeded 15. Furthermore, 3Pd–MoO₃ demonstrated a fast response time of less than 2 min, thereby highlighting its high potential for the early detection of hydrogen gas leaks. The color shift of 3Pd–MoO₃ from light brown to dark gray in the presence of hydrogen was attributable to the combined effects of the color changes in both MoO₃ and Pd. With further improvements in performance, particularly in terms of the sensing speed, the 3Pd–MoO₃ nanowires could be highly effective for real-time hydrogen gas leak detection in industrial settings, wherein safety and prompt intervention are essential.

ACKNOWLEDGMENT

This research was supported by the Korea Institute of Marine Science and Technology Promotion (KIMST) funded by the Ministry of Oceans and Fisheries (RS-2023-00239826). This work was also supported by the “Cooperative Research Program for Agriculture Science and Technology Development (Project No. PJ016994)” Rural Development Administration, Republic of Korea.

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