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Gasochromic Tungsten Oxide Thin films for Hydrogen Monitoring in Natural Gas

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Summary:
In this study we reported a gasochromic sensor for detecting hydrogen in natural gas, utilizing a tungsten oxide thin film coated with platinum nanoparticles. The sensor demonstrated excellent accuracy and repeatability in hydrogen detection within a methane environment, along with significant long-term stability. This advancement enhances the reliability of gas detection technologies for improved safety and efficiency.

Keywords: natural gas, methane, hydrogen, optical sensor, gasochromism, tungsten oxide, platinum nanoparticles, sol-gel

Background, Motivation an Objective

Natural gas represents a crucial element in the global energy supply; however, there is an increasing attention on renewable energy sources, particularly hydrogen, to mitigate climate change impacts. Blending hydrogen into existing natural gas pipelines is regarded as one of the most cost-effective approaches to reduce carbon emissions without requiring substantial changes for consumers [1]. To ensure precision in hydrogen dosing and to maintain the quality of the gas, it is essential to accurately measure hydrogen concentrations in natural gas. Several types of hydrogen sensors have been developed, including gas chromatographs and thermal conductivity detectors. However, these technologies often present challenges, such as high costs or operational limitations. Considering that natural gas is a complex mixture composed of components such as methane, ethane, and non-combustible gases like carbon dioxide and nitrogen, there is a pressing need for advancements in detection methods.

In this contest, we have developed a gasochromic sensor for hydrogen detection in natural gas using tungsten oxide (WO_3) thin films. When these films are coated with a metal catalyst like platinum, palladium, or gold, they undergo a color change from transparent to blue upon exposure to hydrogen. This change occurs as molecular hydrogen dissociates and alters the valence state of tungsten, resulting in the formation of tungsten bronze (HxWO3), which leads to the color shift [2]. This material serves as an effective optical transducer for hydrogen sensing. Previous research has shown that platinum-coated tungsten oxide demonstrates excellent performance in detecting hydrogen in air, nitrogen and in argon [3], making it a promising candidate for applications in hydrogen detection within natural gas systems.

Description of the New Method or System

WO_3 thin films were prepared using a sol-gel synthesis method with peroxotungstic acid as the precursor [3]. The sol-gel solution was spin-coated onto fused silica substrates at 2000 rpm for 30 seconds and then annealed at 550°C for 2 hours in air. Platinum (Pt) nanoparticles, synthesized using the polyol method, were deposited onto the WO_3 thin film through spin coating, followed by a treatment at 250°C for 10 minutes. X-ray diffraction (XRD) and scanning electron microscopy (SEM) characterizations confirmed the crystallization of the films. Pt nanoparticles uniformly covered the entire film, with an estimated surface coverage of 37% and an average diameter of 11 nm. (Figure 1).

Gas sensing tests were conducted by analyzing the absorbance changes induced by hydrogen in the 350-900 nm range. A Harrick gas flow cell was used in conjunction with a spectrophotometer at an operative temperature of 200°C. Time-resolved optical responses were recorded at a fixed wavelength of 850 nm. Preliminary investigations were performed with hydrogen balanced in methane to demonstrate the effective response in a reducing atmosphere.

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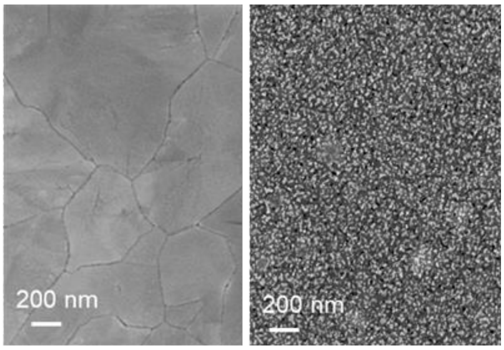

Fig. 1. SEM images of pristine WO_3 film (left) and Pt-coated WO_3 film (right).

Results

When exposed to hydrogen, the Pt-coated WO3 sample turns from transparent to blue, indicating an increase in absorbance at the edge of the visible spectrum. By monitoring the changes at 850 nm, we were able to evaluate the sensing performance of the films. We first investigated the optical response to 5% (v/v) hydrogen in methane, increasing the operating temperature (OT) from 100 °C to 200 °C. As reported in Figure 2, the best response and recovery times (1 second and 58 seconds, respectively) were achieved at 200 °C. This suggests that the bleaching mechanism in the absence of air is the decomposition of tungsten bronze, which can only occur at temperatures above 176 °C [2].

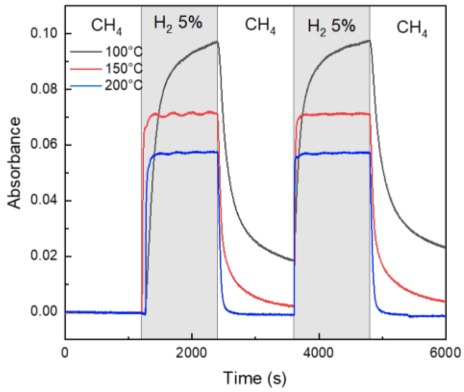

Fig. 2. Dynamic response at 850 nm Pt-coated WO3 sample collected at various temperatures under cycles methane – 5% H2 in methane.

The sensor's response exhibited a linear correlation with hydrogen concentrations ranging from 1% to 20% v/v (maximum concentration allowed in the pipeline), with a coefficient of determination (R^2) of 99.6%. We also tested the repeatability and long-term stability of the sensor. The sample was subjected to 5% and 10% (v/v) concentrations of hydrogen in methane over more than ten cycles, demonstrating excellent signal repeatability with variations in absorbance of less than 1% for all tested concentrations. Additionally, the dynamic response of the sample was maintained even after being stored for one month in a simulated pipeline environment containing hydrogen in methane.

As previously mentioned, natural gas consists not only of methane but also of other hydrocarbons, diluents, and inert gases. Therefore, the sensor was also tested with natural gas. **T**he sensor performs similarly in both methane and natural gas, with comparable response times and maximum absorbance changes. However, the recovery time increases due to the slower bleaching kinetics in the presence of other natural gas components. No cross-sensitivity was observed with any components of natural gas.

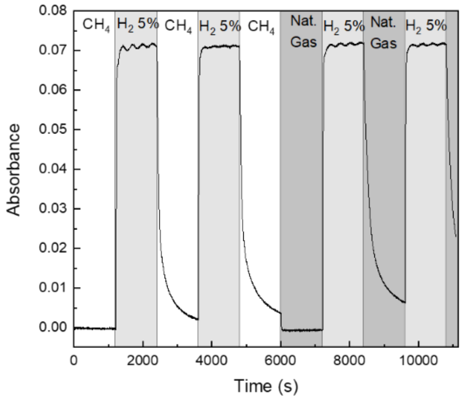

Fig. 3. Dynamic response for Pt-WO3 collected at 200°C under two cycles methane – 5% H2 in methane – methane and two cycles natural gas – 5% H2 in natural gas – natural gas.

The sensor's performance was found to be relatively independent of gas flow.

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