

Selective Benzene Gas Sensing with Flame-made Polytungstate Porous Film

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Summary:

Polytungstates are materials composed of highly oxidized tungsten polyhedral displaying a wide range of applicability due to their tunability. Their usual synthesis routes involve long reaction times and high temperatures, limiting their scalable production. In our work, we use flame aerosol, a rapid and scalable production method, to synthesize nanoparticulate powders and thin porous films. When used as gas sensors for air quality monitoring, these films are highly selective to benzene, even detecting concentrations down to 200 parts-per-billion while operated at 170 °C under 20% relative humidity.

Keywords: polytungstate nanoparticles, chemoresistive gas sensors, porous film, air quality monitoring, aerosol combustion.

Background, Motivation and Objective

Polytungstates are complex tungsten-oxide frameworks composed of edge- and corner-sharing WO_x polyhedra, widely studied for biomedical and functional applications. In particular, WO_6 octahedra can form hexagonal channel structures capable of incorporating alkali or other cations, enabling materials with promising uses in sensing. However, conventional synthesis routes (hydrothermal, solvothermal, and solid-state reaction) are limited by long reaction times, high temperatures, and poor scalability. Additionally, these routes can lead to micron-sized particles due to sintering effects [1], resulting in a loss of sensing performances.

Flame spray pyrolysis (FSP) is a one-step dry aerosol production method for nanoparticulate powders and thin film. It relies on the gas-solid conversion of the aerosol to form agglomerated particles that can be collected either on a filter or by thermophoresis on a sensing substrate to form highly porous films [2].

In our work [3], we leverage FSP technology to produce the pure phase polytungstate $\text{K}_2\text{W}_7\text{O}_{22}$ and determine the role of the production operational parameters on the sizes and composition of the particles produced. When deposited as a porous film, $\text{K}_2\text{W}_7\text{O}_{22}$ showed promising sensing performance for the detection of benzene.

Description of the New Method or System

Nanoparticles of $\text{K}_2\text{W}_7\text{O}_{22}$ have been produced for the first time by FSP. Additionally, their chemoresistive properties when used as porous

film for the detection of benzene have been observed and reported.

Results

Figure 1 shows the X-Ray Diffractometer (XRD) patterns of various powder prepared by FSP for different precursor compositions, labelled by their potassium to tungsten atomic ratios (K/W). For $\text{K/W} = 0.0$, only ϵ - and γ - WO_3 are identified, as expected from literature [4]. As K/W increases, peaks attributed to $\text{K}_2\text{W}_7\text{O}_{22}$ emerge, while those attributed to WO_3 polymorphs shrink. At $\text{K/W} = 0.29$, only pure $\text{K}_2\text{W}_7\text{O}_{22}$ is identified as expected by its stoichiometric composition. Until $\text{K/W} = 0.6$, $\text{K}_2\text{W}_7\text{O}_{22}$ remains the only crystalline phase visible in the XRD, suggesting a high solubility of the potassium without disruption of the crystalline organization. When the stoichiometry is extended to $\text{K/W} = 0.8$ and 1, the $\text{K}_2\text{W}_7\text{O}_{22}$ peaks vanish and only large humps are observed, suggesting an amorphization of the powder.

Pure $\text{K}_2\text{W}_7\text{O}_{22}$ ($\text{K/W} = 0.29$) nanocrystals were directly deposited by thermophoresis onto a water-cooled sensing substrate to form a highly porous film (Fig. 2a). When operated at 170°C under an air flow at 20% relative humidity, the porous film was able to detect benzene concentrations from 2.5 parts-per-million (ppm) down to 0.2 ppm (Fig. 2b). This sensibility is of importance as benzene is a highly toxic air pollutant for which there are no safe levels of exposure according to the World Health Organization. Additionally, our sensor shows good selectivity over a wide range of analytes (Fig. 2c). In particular, the selectivity towards chemically similar

compounds xylene (18.7) and toluene (20.9) is substantially higher than other metal oxide-based sensors (e.g., [5]). Other sensing systems were able to better discriminate these three compounds, but usually really on additional elements such as filters [6] to increase the selectivity.

Illustrations, Graphs, and Photographs

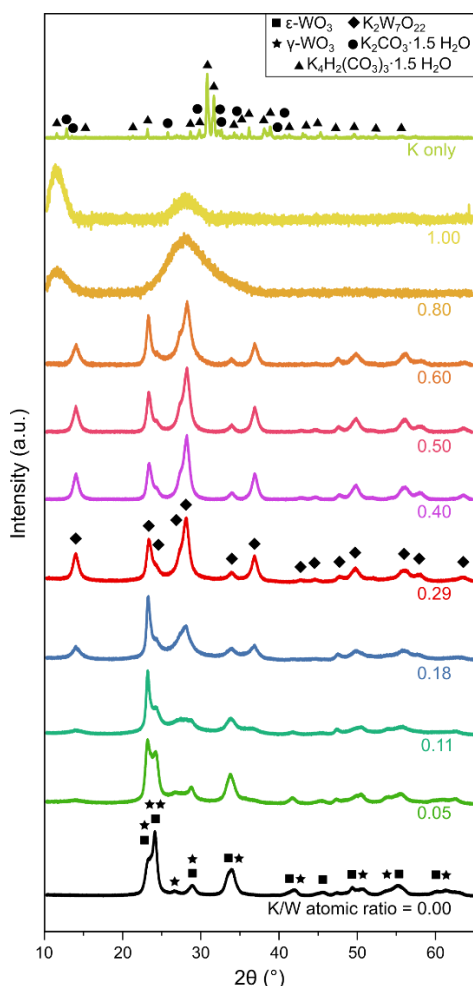


Fig. 1. (a) XRD patterns of nanoparticulate powders obtained by FSP for different K/W ratio. Reproduced from [3].

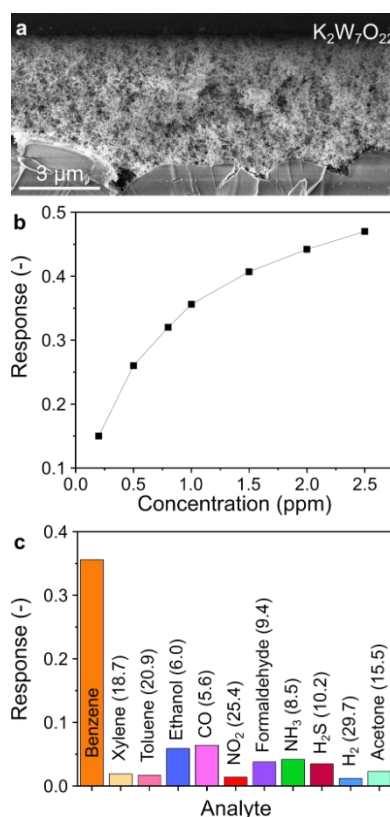


Fig. 2. (a) Scanning electron microscopy image of a porous $K_2W_7O_{22}$ sensing film. Response of a $K_2W_7O_{22}$ sensing film operated at 170°C under an air flow at 20% RH to various (b) benzene concentrations and (c) analytes at 1 ppm. Reproduced from [3].

References

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