

# Ferrochromic WO<sub>3</sub> Nanoparticles for Metabolic Sensors

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## Abstract:

Flame spray pyrolysis (FSP) synthesized  $\epsilon$ -WO<sub>3</sub> nanoparticles has previously been shown by our group to be a selective chemi-resistive sensor for acetone. The proposed mechanism for the sensitivity and selectivity of the sensor has been the interaction between the ferroelectric dipoles of the  $\epsilon$ -WO<sub>3</sub> crystal and the polar acetone molecules. The study of ferroelectric properties of nanoparticles is not a trivial task. The transformative potential of  $\epsilon$ -WO<sub>3</sub> as a ketosis sensor for diabetics and a metabolic rate sensor for diet and exercise monitoring among others, makes it imperative to fully characterize the material so as to achieve optimized properties. Here we report on a visible and reversible color switching phenomenon that is also driven by the ferroelectric structure of the  $\epsilon$ -WO<sub>3</sub>. Previous Raman studies shown by our group suggests that material is not undergoing intercalation and changes color without the need for an electrolyte. Furthermore, we have shown that this coloration appears on glass, alumina, and paper substrates. Thus, it is argued that the FSP-processed  $\epsilon$ -WO<sub>3</sub> exhibits ferroelectricity and that the reversible coloration is not an electrochromic effect but a “ferrochromic” effect; i.e. coloration driven by ferroelectricity.

**Key words:** Sensors, Ferroelectric, WO<sub>3</sub>, Electrochromic, Flame Spray Pyrolysis

## Introduction

Tungsten trioxide (WO<sub>3</sub>) has been shown to exhibit a range of solid-to-solid phase transformations upon cooling, many of which are also accompanied by a decrease in crystallographic symmetry. Upon cooling to -43°C, bulk WO<sub>3</sub> experiences an acentric phase transformation into the monoclinic Pc structure which is often referred to as the epsilon ( $\epsilon$ ) phase [1]. The presence of this acentric crystal structure, as well as numerous reports indicating the presence of an electrical hysteresis, suggests some degree of polarizability of the material and seems to suggest that the epsilon phase of WO<sub>3</sub> is ferroelectric [1, 2].

This low temperature  $\epsilon$ -WO<sub>3</sub> is of particular interest because of it has been shown to be a highly sensitive and selective sensing element for acetone detection [3]. As acetone (in breath and skin emissions) is a biomarker for the monitoring of diabetes through ketosis as well as other metabolic reactions. It is therefore of immense interest to understand what binds it specifically to the ferroelectric polymorph of tungsten trioxide [4]. The reason for the sensitivity and selectivity of the  $\epsilon$ -WO<sub>3</sub> is thought to be due to its ferroelectric nature which favors

the polar acetone molecule [5]. The degree of ferroelectricity in nanometer sized  $\epsilon$ -WO<sub>3</sub> has not been quantified by direct measurement techniques, yet it controls the sensitivity, selectivity, and response of the sensors based on them.

In addition to being a ferroelectric material, WO<sub>3</sub> is also a known electrochromic material. While there is some debate as to the exact mechanism which results in the coloration, it is generally agreed that a redistribution of charge within the electronic structure of the material gives rise to the coloration. To stabilize this redistribution, electrochromic devices use the intercalation of ions to balance the injected charge [6]. During poling of a ferroelectric material, a displacement of an atom occurs which gives rise to a redistribution of electrical dipoles. The final result is a redistribution of charge. We have observed a reversible coloration effect that persists for over a day when the voltage is removed without the need for intercalation. We propose that the coloration switching is coupled with the ferroelectric poling further supporting the previous break-through findings by our group regarding FSP  $\epsilon$ -WO<sub>3</sub> being ferroelectric and a selective acetone sensing material.

## Experimental

The  $\epsilon$ -WO<sub>3</sub> was prepared using TETHIS FSP (NPS10) device. Sensors were prepared by drop coating a suspension of  $\epsilon$ -WO<sub>3</sub> and 1-Heptanol (purity 99%;Sigma Aldrich) onto an alumina substrate (CoorsTek ADS-996) with gold interdigitated electrodes (Case Western EDC #102), glass slide & paper cut out with silver (Ted Pella "Leitsilber" Conductive Silver Cement) printed electrodes.

## Results

The original color of the films before the application of a voltage was a yellow-green color Figure 1. For the alumina sensor, after 10 V was sourced to the electrode the gradual appearance of a localized dark coloration could be seen above the arm connected with the negative terminal. When the leads are switched (akin to changing the direction of the electric field) the coloration disappears from its current state and localizes on the opposite arm which is now the new negative terminal [7].

When 80V was sourced to the alumina sensor, the dark coloration was no longer localized on the negative electrode and spread throughout the sensor. A similar result was observed for the glass and paper sensors, Figure 2. When the alumina sensor was left to sit over night, the original coloration returned. When the 80V was supplied to the glass and paper sensors, the coloration persisted indefinitely without the need of an ion storage layer nor electrolyte.

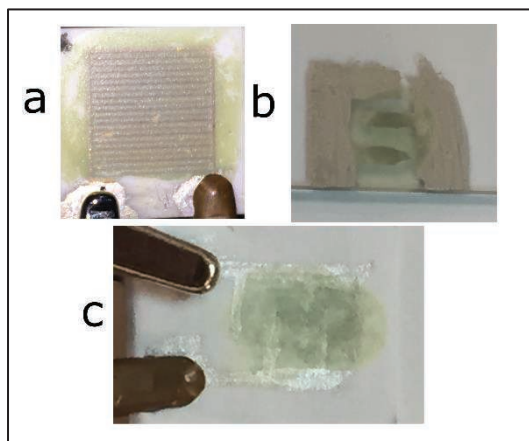


Fig. 1. Original film before testing (a), alumina sensor (b), glass sensor (c) paper sensor

## Discussion and Conclusion

WO<sub>3</sub> is capable of being intercalated by a number of different ions including gold which was present on the electrode. However, when these atoms are injected into the WO<sub>3</sub> matrix, they distort the structure. As such, Raman spectroscopy is a powerful tool in resolving this phenomena due to its sensitivity to chemical

bonding [3]. However, previously published Raman spectroscopy on these samples show no sign of gold or silver intercalation [7].

Furthermore, this coloration occurs regardless of the substrate that the material is on. Thus, it is argued that the FSP-processed  $\epsilon$ -WO<sub>3</sub> exhibits ferroelectricity and that the reversible coloration is not an electrochromic effect but a "ferrochromic" effect; i.e. coloration driven by ferroelectricity. As traditional electrochromic devices consist of an ion storage layer as well as an electrolyte, the commercialization potential of chromic devices consisting of  $\epsilon$ -WO<sub>3</sub> is apparent as it reduces the functional components from three to one while eliminating the use of potentially harmful electrolytes and ion storage layers.

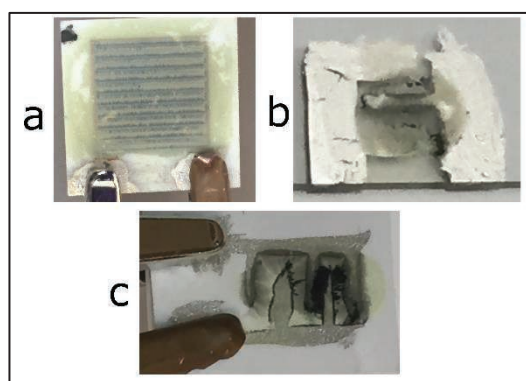


Fig. 2. Colored films after testing (a), alumina sensor (b), glass sensor (c) paper sensor

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