Effect of (100) and (001) Hexagonal \( \text{WO}_3 \) Faceting on Isoprene and Acetone Gas Selectivity

Owen O. Abe 1, Zanlin Qiu 1, Joerg R. Jinschek 1, 2, * and Pelagia-Irene Gouma 1, 2, *

1 Department of Materials Science and Engineering, The Ohio State University, Columbus, OH 43202, USA; abe.24@osu.edu (O.O.A.); qiu.512@osu.edu (Z.Q.); jinschek.1@osu.edu (J.R.J.)
2 Department of Mechanical and Aerospace Engineering, The Ohio State University, Columbus, OH 43202, USA
* Correspondence: gouma.2@osu.edu; Tel.: +1-614-292-4391

Abstract: The hexagonal \( \text{WO}_3 \) polymorph, \( h-\text{WO}_3 \), has attracted attention due to its interatomic channels, allowing for a greater degree of intercalation compared to other \( \text{WO}_3 \) polymorphs. Our research group has previously demonstrated \( h-\text{WO}_3 \) to be a highly sensitive gas sensing material for a flu biomarker, isoprene. In this work, the gas sensing performance of this polymorph has been further investigated in two distinct configurations of the material produced by different processing routes. The first sample was synthesized using \( \text{Na}_3\text{WO}_4 \cdot 2\text{H}_2\text{O} \) and showed (100) faceting. The second sample was synthesized using \( \text{WCl}_6 \) and showed (001) faceting. The gas sensing response of the nanostructured films deposited using the (100) textured \( h-\text{WO}_3 \) sample 1 had a higher response to acetone at \( 350 \, ^\circ \text{C} \). The (001) textured \( h-\text{WO}_3 \) sample 2 favored isoprene at \( 350 \, ^\circ \text{C} \). The selectivity of the latter to isoprene is explained in terms of the dangling bonds present on the (001) facets. The tungsten and oxygen dangling bonds present on the (001) plane favor the adsorption of the isoprene molecule over that of the acetone molecule due to the oxygen containing dipole present in the acetone molecule.

Keywords: metal oxide; gas sensing; hexagonal tungsten trioxide; isoprene; acetone; solvothermal; hydrothermal; crystal facet

1. Introduction

\( \text{WO}_3 \) is an important semiconducting binary metal oxide that can be found in at least seven different polymorphic configurations. Of these, at least six belong to uniquely distinct crystal systems. In the bulk, the thermodynamically stable polymorphs from low temperature to high temperature are as follows: monoclinic \( \text{Pc} \) (\( \varepsilon \) phase) from 0–230 K; triclinic \( \text{Pt} \) (\( \delta \) phase) from 230–290 K; monoclinic \( \text{P}_{21/n} \) (\( \gamma \) phase) from 290–600 K; orthorhombic \( \text{Pmn} \) (\( \beta \) phase) from 600–1170 K; and tetragonal \( \text{P}_{4nm} \) (\( \alpha \) phase) from 1010–1170 K [1]. In addition to these polymorphs, there also exists a kinetically stable hexagonal configuration and a kinetically stable cubic configuration [2]. The hexagonal \( \text{WO}_3 \) (\( h-\text{WO}_3 \)) is a metastable polymorph of \( \text{WO}_3 \), which was first reported in the late 70 s [3]. Due to its hexagonal structure, the \( h-\text{WO}_3 \) has been shown to possess a large network of interatomic channels along the \( c \)-axis [4].

The original synthesis method for obtaining \( h-\text{WO}_3 \) utilized an acid precipitation method of sodium tungstic acid dihydrate [3]. For a time, this was the only successful method in forming this material, and it was thought that the residual sodium in the material acted as a structure directing agent necessary for promoting the growth of the hexagonal structure [3]. This was further supported by the inability of numerous researchers to form \( h-\text{WO}_3 \) from sodium free \( \text{H}_x\text{WO}_y \) compounds. Over the years, additional researchers have been able to form \( h-\text{WO}_3 \) from a variety of precursors including ammonium para-tungstate, tungsten hexachloride, and tungsten foils [4,6–8]. Furthermore, \( h-\text{WO}_3 \) has been reported in a variety of different morphologies ranging from platelets and rods to flowers [9]. The functionality of these different morphologies has been studied for a variety
of different fields including metal oxide (MOx) gas sensors with varying results. Often, researchers attribute their findings to the new improved morphology developed. However, the morphology changes from reference-to-reference, and the gaseous analyte detected also differs; thus, it is difficult to understand the underlying operating mechanism controlling the sensing response with respect to a particular gaseous analyte.

As metal oxide gas sensing is a surface driven phenomenon, typically involving the adsorption of a gaseous analyte onto the surface of the MOx, the properties of the exposed surface strongly impact the overall gas sensing performance [10]. Jian et al. demonstrated the significance of sample faceting by studying the adsorption of various organic dyes onto h-WO3 nanorods synthesized to exhibit (001) and (110) faceting [9]. In their work, they demonstrated that dye adsorption of the (110) material was nearly three times as high as the (001) material [9]. Jia et al. synthesized h-WO3 nanorods with (002) faceting and (100) faceting for MOx gas sensing towards acetone and ethanol [11]. In their work, they demonstrated that at 280 °C, the response towards ethanol was higher for the (100) faceted nanorods, while the (002) faceted nanorods responded better towards acetone [11]. Wu et al. studied the h-WO3 (001) and (110) facets using density functional theory (DFT) and found that the (001) facet is insensitive to methane, while the (110) facet allows for a large amount of electron transfer upon exposure due to coordination of the W and O bonds on the surface [12]. Isoprene being a biomarker for flu makes understanding its gas sensing properties even more appealing [13–16].

To investigate this further, two configurations of h-WO3 were synthesized, one via a solvothermal process and another using a hydrothermal process. Both synthesis routes produced crystalline nanopowders exhibiting a platelet morphology with one exhibiting primarily with (001) facet texturing while the other exhibiting primarily (100) facet texturing. The gas sensing response of the materials towards acetone and isoprene was studied in tube furnace style gas flow bench. A possible mechanism for the difference in their respective gas sensing responses is provided herein.

2. Materials and Methods

An acid precipitation method was used to synthesize the randomly oriented h-WO3 used in this study [17]. The starting materials consisted of Na2WO4·2H2O (Sigma Aldrich) and hydrochloric acid, HCl (Alfa Aesar 36.5–38%). The process was as follows: 1.17 g of Na2WO4·2H2O was dissolved in 17 mL of deionized water, sonicated for 20 min, and then placed in an ice bath and allowed to cool for 60 min. Concurrently, 8.4 mL of HCl (18% in excess of equimolar reaction) was also allowed to cool in an ice bath for 60 min. After several hours, the cooled HCl acid was added to the cooled aqueous Na2WO4·2H2O mixture in one dose. During this time, the mixture gelated almost instantly and turned white. This solution gradually turned from white to lemon cake yellow, and the mixture was allowed to age for 24 h in an ice bath.

At this point, deionized water was added to the mixture, and it was gently stirred with a glass rod. Afterwards the mixture was centrifuged, and the precipitate was removed and washed several times with deionized water to remove excessive sodium and chloride ions. Afterwards the washed tungstic acid precipitate was allowed to dry overnight, the precipitate was added to a Teflon lined hydrothermal pressure vessel (Parr Instruments 4700 Series 45 mL). The pressure vessel was filled to 90% with deionized water and placed in an oven for twelve hours at 120 °C. During this time, hydrothermal dehydration of the tungstic acid occurred at subcritical autogenous pressures to form WO3·½H2O via WO3·intraparticle dehydration. The as-received material was centrifuged and washed with deionized water several times and allowed to dry at room temperature in a fume hood. The remaining material was heat treated at 350 °C for two hours to obtain the final h-WO3 product.

This acid precipitation route and hydrothermal dehydration can be described by the following series of reactions:
a) \( \text{Na}_2 \text{WO}_4 \cdot 2\text{H}_2\text{O} \) dissociation in an alkaline aqueous

\[
\begin{align*}
\text{Aqueous Dissociation} \\
\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} & \rightarrow 2\text{Na}^+ + [\text{WO}_4]^{2-} + 2\text{H}_2\text{O}
\end{align*}
\]

b) Precipitation of \( \text{H}_2\text{WO}_4 \) in hydrochloric acid

\[
\begin{align*}
\text{Aqueous Acid Precipitation} \\
2\text{Na}^+ + [\text{WO}_4]^{2-} + \text{H}_2\text{O} + 2\text{HCl} & \rightarrow \text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O} + 2\text{Na}^+ + 2\text{Cl}^-
\end{align*}
\]

c) Self-ionization of water to produce \( \text{OH}^- + \text{H}^+ \) ions

\[
\begin{align*}
\text{Self Ionization} \\
\text{H}_2\text{O} & \rightarrow \text{OH}^- + \text{H}^+
\end{align*}
\]

d) Hydrothermal dehydration of crystalline water by subcritical water

\[
\begin{align*}
\text{Hydrothermal Dehydration} \\
3[\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}] + \text{OH}^- + \text{H}^+ & \rightarrow 3[\text{WO}_3 \cdot \frac{1}{3}\text{H}_2\text{O}] + 6\text{H}_2\text{O}
\end{align*}
\]

e) Thermal dehydration of product at 350 °C to form anhydrous \( h\)-\( \text{WO}_3 \)

\[
\begin{align*}
\text{Thermal Dehydration} \\
\text{WO}_3 \cdot \frac{1}{3}\text{H}_2\text{O} & \rightarrow h - \text{WO}_3
\end{align*}
\]

A chloride based solvolysis method was performed to synthesize the \( (001) \) \( h\)-\( \text{WO}_3 \) [18]. Starting materials consisted of \( \text{WCl}_6 \) (Sigma-Aldrich; St. Louis, MO, USA) and ethanol anhydrous (Sigma-Aldrich). The solvolysis method was performed in an argon filled glove box to prevent hydration of the \( \text{WCl}_6 \) precursor. The process was as follows: 100 mL of ethanol anhydrous was heated to 70 °C under constant magnetic stirring; 3.95 g of \( \text{WCl}_6 \) was added to this solution in one dose under magnetic stirring to create a 0.1 M solution of tungsten alkoxychloride. Upon addition of the \( \text{WCl}_6 \), the solution immediately turns yellow as HCl vapor is emitted from the container. Eventually the solution turns red, clear, and blue, and ultimately arrives at a deep green color after one week of aging. During this solvolysis process and aging, substitution of the chlorine ligand for the ethoxy ligand results in a change in coordination of the tungsten alkoxychloride, which is reflected in its color.

After the solution has aged for one week, 10 mL of the green tungsten alkoxychloride was removed from the argon filled glovebox and added to 10 mL of distilled water. The mixture immediately turned blue, indicating the onset of hydrolysis of the tungsten alkoxychloride into the dark blue amorphous \( \text{WO}_3 \) monohydrate. The colloidal mixture was allowed to age under magnetic stirring for three hours to ensure hydration and then transferred to a Teflon lined hydrothermal pressure vessel (Parr Instruments 4700 Series 45 mL) and heated for twelve hours at 200 °C from room temperature at a ramp rate of 3 °C per min. During this ramping time, hydration of the tungsten alkoxychloride was accelerated via reaction with the existing water and hydrothermal decomposition of the ethoxy groups, further increasing the concentration of water in the system. As the temperature increases, self-ionization of the water occurs, which in turn enables the hydrothermal dehydration of the \( \text{WO}_3 \) hydrate via intraparticle dehydration to form \( \text{WO}_3 \cdot \frac{1}{3}\text{H}_2\text{O} \).
The as-received material was light blue, and it was centrifuged and washed with deionized water and ethanol several times, during which the organics washed away and revealed an off-white powder. This powder was allowed to dry at room temperature in a fume hood. The material was then heat treated at 350 °C for 2 h to obtain the final h-WO3 product.

This solvolysis route and solvothermal synthesis route can be described be the following series of reactions:

a) Solvolysis of WCl6 in anhydrous ethanol

\[ WCl_6 + nC_2H_5OH \rightarrow W(OC_2H_5)_nCl_{n-6} + nHCl \]

b) Hydration of tungsten alkoxychloride to form WO3·H2O

\[ W(OC_2H_5)_nCl_{n-6} + nHCl + H_2O_{\text{Hydrolysis}} \rightarrow WO_3·H_2O + nHCl + (n - 6)C_2H_5OH \]

c) Hydrothermal decomposition of ethanol to form excess water and ethylene

\[ C_2H_5OH \rightarrow C_2H_4 + H_2O \]

d) Self-Ionization of water to produce OH− + H+ ions

\[ H_2O \rightarrow OH^- + H^+ \]

e) Hydrothermal dehydration of crystalline water by subcritical water

\[ 3[H_2WO_4] + OH^- + H^+ \rightarrow 3 \left[ WO_3·\frac{1}{3}H_2O \right] + 3H_2O \]

Gas sensors were prepared by mixing 0.01 g of the heat-treated h-WO3 powders with 1 mL of 2-heptanol and drop coating 1 µL of the suspension onto interdigitated electrodes to form the sensing film and allowed to dry overnight. These electrodes consisted of an alumina substrate with interdigitated platinum “fingers” and gold wire leads [19]. Electrical connections to the digital multimeter were established via the gold leads, and the gas sensing response of the sensors were studied using a custom gas flow bench consisting of a tube furnace (Lindberg/Blue), MKS 1179a mass flow controllers, and an MKS 247D power supply. Gas sensing experiments were conducted in 500 sccm OSHA grade D breathing air with a relative humidity of less than 0.1% [19]. The crystal structure of the materials was determined using X-ray powder diffractionmetry (XRD Bruker D8). The sample morphology was assessed through the use of transmission electron microscopy (TEM FEI Tecnai G2 30 TWIN). Analysis of micrographs were conducted using the ImageJ software.

3. Results
3.1. Crystal Structure

Figure 1 shows the X-ray diffraction (XRD) spectra of the h-WO3 samples synthesized in this work using the Na2WO4·2H2O and WCl6 precursors. Both patterns are well indexed to the typical diffraction peak profile of the h-WO3 standard reference pattern (ICSD 32001).
Figure 1. XRD spectra of the standard reference pattern (ICSD 32001 from Ref. [3]) for the hexagonal polymorph of tungsten trioxide (h-WO₃) in comparison to the h-WO₃ samples synthesized in this work using the Na₂WO₄·2H₂O and WCl₆ precursors.

For the Na₂WO₄·2H₂O sample, the relative intensity of the (100) peak compared with the (001) peak is stronger than what is reported in the standard reference pattern. However, for the WCl₆ h-WO₃ sample, the relative intensity (001) peak compared with the (100) peak is significantly stronger than what is reported in both the standard reference pattern and the Na₂WO₄·2H₂O h-WO₃ pattern. This observation is the indicative of crystal facet exposure.

The relative texture coefficient of a specific crystal facet, TC(hkl), was used to evaluate the degree of crystal facet exposure in the Na₂WO₄·2H₂O and WCl₆ synthesized h-WO₃ samples. The texture coefficients of the (001) and (100) facets are given by the following equations [11]:

$$TC_{001} = \frac{I_{001}/I_{001}^{0}}{I_{001}/I_{001}^{0} + I_{100}/I_{100}^{0}}$$
$$TC_{100} = \frac{I_{100}/I_{100}^{0}}{I_{001}/I_{001}^{0} + I_{100}/I_{100}^{0}}$$

where TC_{001} and TC_{100} are the relative texture coefficients of the diffraction peaks of (001) over (100) and (100) over (001), respectively. I₀₀₁ and I₁₀₀ are the measured diffraction peak intensities from the XRD patterns in Figure 1 of the Na₂WO₄·2H₂O and WCl₆ synthesized h-WO₃ samples. I₀₀₁₀₀ and I₁₀₀₀₀ are the corresponding values of the standard reference pattern from a randomly oriented sample of h-WO₃. The texture coefficients for the samples can be found in Table 1. From this, it can be seen that the TC_{001} for the WCl₆ h-WO₃ sample is 0.75, indicating that this sample has mainly (001) facets exposed. The TC_{100} for the Na₂WO₄·2H₂O sample is 0.66, indicating that this sample has mainly exposed with (100) facets (Note: The texture coefficient of a randomly oriented sample is 0.5, indicating its randomness).
Table 1. Texture coefficients for the 001 and 100 facets of the Na$_2$WO$_4$·2H$_2$O and WCl$_6$ synthesized h-WO$_3$ samples.

| Sample                | TC$_{001}$ | TC$_{100}$ |
|-----------------------|------------|------------|
| WCl$_6$ h-WO$_3$      | 0.75       | 0.25       |
| Na$_2$WO$_4$·2H$_2$O h-WO$_3$ | 0.34   | 0.66       |

3.2. Crystal Morphology

Transmission electron microscopy (TEM) micrographs of a crystallite from the WCl$_6$ h-WO$_3$ sample can be seen in Figure 2a and consist of large flat faceted platelets with length scales on the order of hundreds of nanometers. The hexagonal features of the sample can clearly be seen by the ≈120° crystal edges. Selected area electron diffraction (SAED) patterns of the WCl$_6$ h-WO$_3$ crystallite can be seen in Figure 2b. These patterns show the material to be highly defect free and to correspond with the [001] zone axis of the hexagonal polymorph of WO$_3$. These results further indicate that the large facet observed in Figure 2a corresponds with the (001) surface.

Figure S1a shows the morphology of the Na$_2$WO$_4$·2H$_2$O sample. The morphology of it is a combination of nanoplates and nanorods (See Supplement). In the Figure S1b, nanoplates with some “feelers” are observed, which suggests that the nanoplates are formed by aggregation of the nanorods. Although some nanorods are present in Figure 2a, crystallites with “feeler” features are not observed. Based on that, it is reasonable to deduce that the 001 facets plates are not the aggregation mechanism mentioned above.

3.3. Gas Sensing

Figure 3a,b show the sensing response at 350 °C for the WCl$_6$ h-WO$_3$ sample towards 1, 2, 3 and 4 ppm of acetone (a) and isoprene (b) gas, respectively. Figure 3c,d show the sensing response at 350 °C for the Na$_2$WO$_4$·2H$_2$O h-WO$_3$ sample towards 1, 2, 3, and 4 ppm acetone (c) and isoprene (d) gas, respectively. The response (R) of the sensors have been calculated using the following equation:

\[ \text{Response (R)} = \frac{R_O}{R_G} \]

where $R_O$ is taken to be the baseline resistance of the sensor and was measured at 350 °C in 500 sccm OSHA grade D breathing air. $R_G$ is taken to be the resistance of the sensor upon exposure to the test gas. In this work, the test gasses are isoprene and acetone. Response vs. concentration plots for the WCl$_6$ h-WO$_3$ and Na$_2$WO$_4$·2H$_2$O h-WO$_3$ samples towards
acetone and isoprene at 350 °C can be seen in Figure 4a,b, respectively. Figure 4 shows that the response of the WCl₆ h-WO₃ consistently exhibited a higher response towards isoprene at every test concentration. This differs from the Na₂WO₄·2H₂O h-WO₃, which exhibited a higher response towards acetone at every test concentration.

To evaluate what the optimal operating temperature is for the sensing material, the response to acetone and isoprene was also evaluated at 250 and 300 °C (in addition to 350 °C) using similar acetone and isoprene concentrations. A plot of the gas sensor response, R, as a function of temperature for the WCl₆ h-WO₃ can be seen in Figure 5.
Figure 4. Comparison of the gas sensing response of the WCl$_6$ h-WO$_3$ sample (a) and the Na$_3$WO$_4$·2H$_2$O sample towards acetone and isoprene at 350 °C for 1, 2, 3 and 4 ppm gas concentrations (b) along with their standard deviations.

Figure 5. Comparison of the gas sensing response for the WCl$_6$ h-WO$_3$ nanstructured films from Figure 3 at 250, 300, and 350 °C towards 4 ppm of acetone and isoprene along with their standard deviations.

4. Discussion

Crystal Morphology

The primary difference between the two synthesis routes for h-WO$_3$ lies in the chemistry of the precursors used, the details of which are unique to the synthesis routes taken, but the final step is always to obtain the WO$_3$·$\frac{1}{2}$H$_2$O precursor. The orthorhombic WO$_3$·$\frac{1}{2}$H$_2$O is an intermediate phase of h-WO$_3$. When subjected to mild thermal heat treatments, this material transforms into an anhydrous h-WO$_3$. When this was initially discovered by Gerand et al., it was not exactly clear as to why the $\frac{1}{2}$ hydrate is the only hydrate of WO$_3$ that forms h-WO$_3$. Work by the author and work reported by other researchers have reported the inability for the monohydrate (1·H$_2$O) or dihydrate (2·H$_2$O) to form h-WO$_3$ when subjected to mild thermal heat treatments [3,20]. Today, it is thought to be uniquely related to the crystal structure of the $\frac{1}{2}$ hydrate compared to that of the higher
order hydrates [21,22]. The crystal structure of the monohydrate and dihydrate consists of corner sharing octahedra with layers of interatomic water alternating with layers of WO$_6$ octahedrons [23]. The dihydrate compares to the monohydrate by the existence of two interatomic water molecules.

The $\frac{1}{2}$ hydrate is also orthorhombic and contains interatomic water molecules, but it is coordinated with WO$_6$ octahedrons and WO$_6$:H$_2$O octahedrons, which average out to an overall hydration composition of $\frac{1}{4}$ [21]. This results in a change in the coordination of the octahedrons, causing a lateral shift of the octahedrons in the a/b plane forming the primary framework for the h-WO$_3$ along the c-axis [22]. When the $\frac{1}{2}$ hydrate is subjected to a mild heat treatment, the orthorhombic WO$_3$: $\frac{1}{4}$H$_2$O transforms into the anhydrous h-WO$_3$ [21,22].

The primary difference between the two anhydrous samples is the large relative intensity of the 001 peak in the WCl$_6$ h-WO$_3$ sample compared to that of the reference sample or the Na$_2$WO$_4$:2H$_2$O h-WO$_3$ prepared in this work. As expected, the TEM micrographs in Figure 2. showed that the large flat surface in the WCl$_6$ h-WO$_3$ crystallite is the (001) surface, and the viewing direction is the [001] direction of the h-WO$_3$ structure. This (001) facet texturing is the reason for the anomalously high relative intensity of the 001 peak in the XRD pattern reported in Figure 1. The texturing coefficient of the WCl$_6$ h-WO$_3$ (001) facet was determined to be 0.75 further, indicating the presence of a highly oriented (001) faceted h-WO$_3$. The texturing coefficient of the Na$_2$WO$_4$:2H$_2$O h-WO$_3$ sample was 0.66 for the (100) facet, further indicating a preferred texturing in this sample which differs from the WCl$_6$ h-WO$_3$.

Examining Figure 4, it can be readily observed that the response of the Na$_2$WO$_4$:2H$_2$O h-WO$_3$ was consistently higher for acetone than isoprene at every concentration tested.

Compared with that of the Na$_2$WO$_4$:2H$_2$O h-WO$_3$, the gas sensing response of the WCl$_6$ h-WO$_3$ was lower overall at every concentration of each gas. Additionally, the response of the (001) h-WO$_3$ towards isoprene is greater than its response towards acetone. This difference in selectivity from acetone to isoprene for the (100) and (001) facet texturing is likely attributed to the different surface properties of the respective planes.

Figure 6a shows the (001) terminated surface h-WO$_3$ structure down the [010] direction and down the [111] direction. This is compared with the (100) terminated surface in Figure 6b down the [001] and [101] viewing directions. For a defect free surface, the (001) surface has only oxygen dangling bonds, whereas the (100) surface has both oxygen and tungsten dangling bonds. Furthermore, for a super cell of identical size, the (100) terminated surface has a higher density of dangling bonds.

Looking at Figures 7 and 8, the structure of the acetone molecule contains an electrical dipole moment pointing towards a lone oxygen atom. The (001) facet of the h-WO$_3$ contains mostly oxygen dangling bonds. As such, the electronegative interaction between
the oxygen dangling bonds and the oxygen dipole would discourage surface interactions across the large (001) faceted surface, which accounts for most of the surface area of the material. This is supported by DFT studies, which indicate that acetone adsorption onto the (001) surface of \( h\text{-WO}_3 \) occurs more favorably through carbon–hydrogen bridging through the oxygen dipole on oxygen deficient surfaces where oxygen vacancies are present [24]. For the (100) facet, one can immediately see a higher density of dangling bonds as well as the presence of tungsten and oxygen dangling bonds. In particular,

\[ \text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} \text{ h-WO}_3 \]

One can see the presence of a bridging oxygen dangling bond, which has been known to be a preferential interaction site for oxygen containing molecules such as acetone [25]. This increase in overall density of dangling bonds on the (100) surface likely attributes to the overall higher response of the \( \text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} \text{ h-WO}_3 \) to acetone compared to the \( \text{WCl}_6 \text{ h-WO}_3 \). Isoprene, while containing carbon and hydrogen atoms, lacks this oxygen containing dipole, which limits its potential adsorption configuration. As such, the material shows a response to isoprene molecule, but a significantly stronger response towards that of the acetone molecule [25,26].

In contrast, the (001) surface, which only contains oxygen dangling bond, and the isoprene molecule, which has only carbon and oxygen atoms, have a wider variety of orientational adsorption [24]. This mechanism is analogous to our previously reported gas sensing mechanism of the ferroelectric \( \varepsilon\text{-WO}_3 \) towards the acetone molecule via its ferroelectric dipole interactions with the polar acetone molecule [19]. As the

Figure 6. Geometrical structures of the (001) terminated surface (a) and the (100) terminated surface (b) from ICSD 32001. Red and grey spheres represent oxygen and tungsten atoms, respectively. The viewing directions for the structures from left to right are [010], [111], [001], and [101].

Figure 7. Potential molecule interaction orientation with the (001) facet of the \( h\text{-WO}_3 \) structure. Red horizontal line indicates the (001) plane. Red and grey spheres represent oxygen and tungsten atoms, respectively.

Figure 8. Potential molecule interaction orientation with the (100) facet of the \( h\text{-WO}_3 \) structure. Red horizontal line indicates the (100) plane. Red and grey spheres represent oxygen and tungsten atoms, respectively.
temperature of the sample increases, acetone desorbs more rapidly from the surface, resulting in a decrease in response as the temperature increases [24]. This has been observed in Figure 5 and is consistent with the reports by other researchers [4,27]. The results reported herein of the (100) facet having a higher response to acetone than the (001) facet differ from the work previously reported by Jia et al., who reported a higher response for the (002) facet as opposed to the (100) facet [11]. However, it should be noted that Jia et al. synthesized hexagonal nanorods, whereas the nanomaterials studied here have platelet shapes. Furthermore, as their paper was focused mainly on ethanol and acetone, they did not report any sensing results on isoprene. It is quite possible that if tested, isoprene would have responded better for their (001) material, as ours did.

5. Conclusions

Two morphologies of $h$-WO$_3$ have been synthesized via a solvothermal and hydrothermal technique. The XRD patterns of the solvothermal material synthesized using WCl$_6$ were dominated by (001) facet texturing and exhibited a preferred orientation (001). The XRD pattern of the hydrothermal material synthesized using Na$_2$WO$_4$·2H$_2$O was dominated by (100) facet texturing and exhibited a higher relative intensity of the 100 diffraction peak. Both samples exhibited a platelet-like morphology, and the SAED pattern of the WCl$_6$ shown confirms the presence of a large (001) terminated surface. The gas sensing behavior of the two materials were conducted at 250, 300, and 350 °C. At 250 °C, the WCl$_6$ $h$-WO$_3$ showed better selectivity towards acetone. Upon increasing the temperature towards 300 °C, the selectivity switched from acetone to isoprene, indicating an increased desorption rate of acetone, which is consistent with the literature. At 350 °C, the WCl$_6$ $h$-WO$_3$ showed an overall lower response to both gases than that of the Na$_2$WO$_4$·2H$_2$O $h$-WO$_3$. It is proposed herein that the cause for this increased selectivity and decreased response is related to the dangling bond configuration of the (001) terminated surface, which contributed to the higher response of the WCl$_6$ $h$-WO$_3$ over that of the Na$_2$WO$_4$·2H$_2$O due to the electronegativity of the surface oxygen and the acetone oxygen dipole. This is contrasted by the isoprene molecules structure, which is less polar and only contains carbon and hydrogen atoms, allowing for a lower adsorption rate. Future work in this area will revolve around improving the overall response of the WCl$_6$ $h$-WO$_3$ by optimizing the synthesis parameters and decreasing the overall particle size to increase the overall performance of the sensor. Overall, the work herein serves as an excellent step towards improving the development of $h$-WO$_3$ towards isoprene for the development of a flu breathalyzer.

Supplementary Materials: The following are available online at https://www.mdpi.com/1424-8220/21/5/1690/s1: Figure S1: (a,b) TEM micrographs of the Na$_2$WO$_4$·2H$_2$O $h$-WO$_3$ sample under different magnification. The red region in Figure S1b contains polytypic features.

Author Contributions: Conceptualization, O.O.A. and P.-I.G.; methodology, O.O.A., and Z.Q.; software, O.O.A., and Z.Q.; validation, O.O.A., Z.Q., J.R.J., and P.-I.G.; formal analysis, O.O.A., Z.Q., J.R.J., and P.-I.G.; investigation, O.O.A., and Z.Q.; resources, J.R.J. and P.-I.G.; data curation, O.O.A., and Z.Q.; writing—original draft preparation, O.O.A., and Z.Q.; writing—review and editing, O.O.A., Z.Q., J.R.J., and P.-I.G.; visualization, O.O.A., and Z.Q.; supervision, J.R.J. and P.-I.G.; project administration, J.R.J. and P.-I.G.; funding acquisition, P.-I.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research has received funding by the Orton Chair Funds and the National Science Foundation award CBET #2029847.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.
