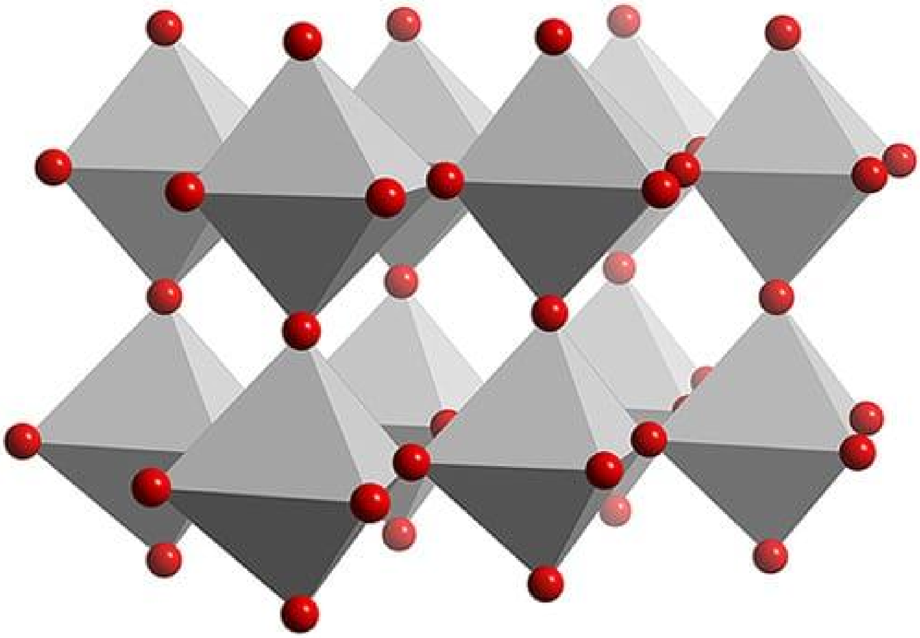
# Tungsten oxides. Structure, properties and applications



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# Abstract

In the last decades, the information regarding Tungsten oxide, its properties and applications have increased rapidly. In this project, peer-reviewed sources have been thoroughly studied and summarized into a readable report of tungsten oxides manufacturing process as well as some of its structures. The most relevant properties for tungsten oxide are also outlined as well as some of the applications that have shown great potential for future development.

The most common manufacturing process that is included revolves around the canceling of ammonium paratungstate tetrahydrate to form $WO_3$. Other manufacturing methods that are briefly discussed are the hydrothermal and solvothermal processes. Tungsten oxide has a wide array of structures which all can be utilized differently, the most common structures being $\gamma$-WO3 and $\delta$-WO3 due to their temperature being intertwined with the earth's temperature.

Properties that are reviewed and studied include tungsten oxides thermal properties, optical properties, and electrical properties. Tungsten oxides properties have given it an unique field of applications. The applications that are covered in this report consists of electrochromic devices such as the “smart  windows”, pH-sensing, gas sensors for hazardous gasses, and photocatalysis

Future work for tungsten oxide shows great promise. This report covers some of the basic information regarding tungsten oxide and follows up with some of the areas that are applicable for tungsten oxide.

# Sammanfattning

Under de senaste decennierna har informationen om volframoxid, dess egenskaper och tillämpningar ökat snabbt. I detta projekt har peer-reviewed källor studerats grundligt och sammanfattats till en läsbar rapport om volframoxider och deras tillverkningsprocess såväl som några av dess strukturer. De mest relevanta egenskaperna för volframoxid beskrivs också samt några av de användningsområden som har visat stor potential för framtida utveckling.

Den vanligaste tillverkningsprocessen som ingår kretsar kring annulleringen av ammonium paravolframat tetrahydrat för att bilda $WO_3$. Andra tillverkningsmetoder som diskuteras kort är de hydrotermiska och solvotermiska processerna. Volframoxid har ett brett utbud av strukturer som alla kan användas på olika sätt, de vanligaste strukturerna är $\gamma$-$WO_3$ och $\delta$-$WO_3$ på grund av deras temperatur är sammanflätad med jordens temperatur.

Egenskaperna som granskas och studeras inkluderar volframoxidens termiska egenskaper, optiska egenskaper och elektriska egenskaper. Volframoxidens egenskaper har gett den ett unikt användningsområde. Applikationerna som behandlas i denna rapport består av elektrokroma enheter som “smarta fönster”, pH-avkänning, sensorer för farliga gaser och fotokatalys.

Framtida arbete för volframoxid ser mycket ljust ut. Denna rapport täcker en del av den grundläggande informationen om volframoxid och följer upp några av de områden som är tillämpbara för volframoxid.

# 1 Introduction

The introduction covers some basic history regarding ceramics in general as well as some key advancements throughout history. A brief preface of tungsten oxide is also given to set the stage for the report.

## 1.1 Background

Ceramics have been used for milleniums by humans, there is evidence that the first ever human-made ceramics were created at least 24 000 years B.C. The key industry was founded when humans learned that clay could be found in abundance and fashioned into items by first combining with water and then fire. With the formation of permanent populations committed to agriculture and farming, the use of pottery increased rapidly during the Neolithic period. Clay-based ceramics became used as containers for water and food, art pieces, tiles and bricks around 9 000 B.C. and its use expanded from Asia to the Middle East and Europe. The creation of the wheel about 3,500 B.C. was one of the earliest achievements in the production of pottery. The invention of the wheel enabled the use of the wheel-forming process to create ceramic objects with radial symmetry.

It has consistently been one of the key materials throughout human history and still is to this day. As technology has progressed, the area of usage for ceramics has expanded along with it. What once was the process of making urns can for example now be the process of designing smart windows or recognizing harmful gasses.

One of many ceramics is tungsten oxide. It is found naturally in hydrates which in organic chemistry is a compound created via hydration, which is defined as "the addition of water or the constituents of water to a molecular entity". Tungsten oxide occurs in many types of stoichiometric variations and every one of them is unique. For example they come in different colors, have different mechanical properties and different thermal properties. Every single composition of tungsten oxide is affected both by its chemical stoichiometry and its structure. Tungsten oxide is therefore applicable in many different types of industries, everything from Smartglass to gas sensors.

Over the last decade, significant advances in composition, crystal structures, morphological control, and composite construction have been achieved to improve optical absorption, charge separation, redox capacity, and electrical conductivity. This family of materials has been used to develop many highly efficient processes and applications such as $CO_2$ reduction, solar-light driven water splitting, and pollutant removal, as well as electrochromism, supercapacitors, lithium batteries, solar and fuel cells, non-volatile memory devices, gas sensors, and cancer therapy. [2]

## 1.2 Purpose and goal

The purpose of this report is to study tungsten oxides, their structure, properties and applications. After which we will then summarize our findings into a report. Our main goal is to deepen our knowledge of ceramics, specifically tungsten oxides by using scientific peer-reviewed sources and also improving our scientific report writing. Side goals for this report is the experience we get from the writing report. This experience is very valuable as we progress in our education and when we for example are to write our thesis, both for our Bachelor's degree as well as for our Master's degree.

## 1.3 Method

In order to reach our goal a thorough base of peer-reviewed sources was required. To find these peer-reviewed sources we used a combination of scientific search engines such as Web of Science, Google Scholar and Primo which is the KTH Library search tool. Through filtering and studying the relevant sources for our project a report summarizing the ones most relevant to our project will be made. When studying a scientific report concentration must be upheld as well as always being ready to look up the meaning of a term or a concept to get the context of the report that is being studied.

# 2 Tungsten oxides

Tungsten oxide is a semiconductor which means that it is a solid material with a conductivity between a metal and an insulator. There are many variants of tungsten oxides. The most common one in the report is $Wo_3$ because it has the most information about it. However there exists extremely many different types of tungsten oxide and all of the different types have their own properties and structures.

## 2.1 Manufacturing

There are many different ways to manufacture tungsten oxide. Probably the most mainstream one is *reaction 1*. Where in this case $WO_3$ is manufactured by canceling ammonium paratungstate tetrahydrate.

$$(NH_4)_{10}(H_2W_{12}O_{42}) \cdot 4H_2O \rightarrow 12WO_3 + 10NH_3 + 10H_2O \qquad \text{(Reaction 1)}$$

A variant of Tungsten oxide that is very used in today's society is $WO_{2.72}$. $WO_{2.72}$ is non stoichiometric and can be synthesized in multiple ways depending on what structure is required. The main factors that change depending what structure you want is the difference in processing and what precursor you use. For example it is possible to use $WO_3$ and W as precursors for chemical vapor transport meanwhile for a solid phase reaction $WCl_6$ and ethanol is used. The processing also differs a lot in the use of temperature between 600-650 C for the chemical vapor transport and 100-800 for the solid phase reaction. Other variables such as time which was in the span of 40 min - 1 hour and what substance they were processed in are also relevant. The different types of substances were Ar, $H_2$ and $N_2$.

Another way to produce the $WO_2$ is by using Hydrothermal or Solvothermal processing. The hydrothermal method is a pretty simple method and uses the pressure, temperature and the precursor as framework. The most used solvent is water in the hydrothermal process. The hydrothermal process has its upsides and downsides as any other process. For example the hydrothermal process uses very high heats under often a long period of time which makes it very energy dependent. You need big quantities of energy in comparison to other processes. Besides the energy consumption, it's seen as a very effective process in the aspects of being friendly for the environment, good dispersion in solution etc. The most commonly used precursors for the hydrothermal process are $H_2WO_4xH_2O$, $Na_2SO_4$, $NaWO_4$ and $(NH_4)_2SO_4$. Solvothermal processing is pretty similar to the hydrothermal one but instead of using water as the solvent it uses ethanol and ethylene glycol. As for every process all the parameters such as temperature, time and precursors change. For the solvothermal the main precursors used are $WCl_6$ and ethanol. The energy consumption problem still remains because of the long times and high temperatures used. [6][12]

## 2.2 Structures

For the crystalline stoichiometrically $WO_3$ it is in most cases built with the use of edge sharing of $WO_6$ (ochtraheda). There are plenty of different structures that the $WO_3$ can take shape in depending on temperature. The following structures are monoclinic II (ε-$WO_3$), triclinic (δ-$WO_3$), monoclinic I (γ-$WO_3$), orthorhombic (β-$WO_3$), tetragonal (α-$WO_3$), hexagonal (h-$WO_3$), and cubic (c-$WO_3$). The Cubic is usually not included experimentally because that is the ideal state for the $WO_3$. The structure of $WO_3$ depends on the slope of $WO_6$ and the rotation where $WO_3$ is the ideal state. In *figure 1* the different structures are shown with the parameters of the Temperature, millers index and charge. There is also different data concerning the lattice constant. [1][2]

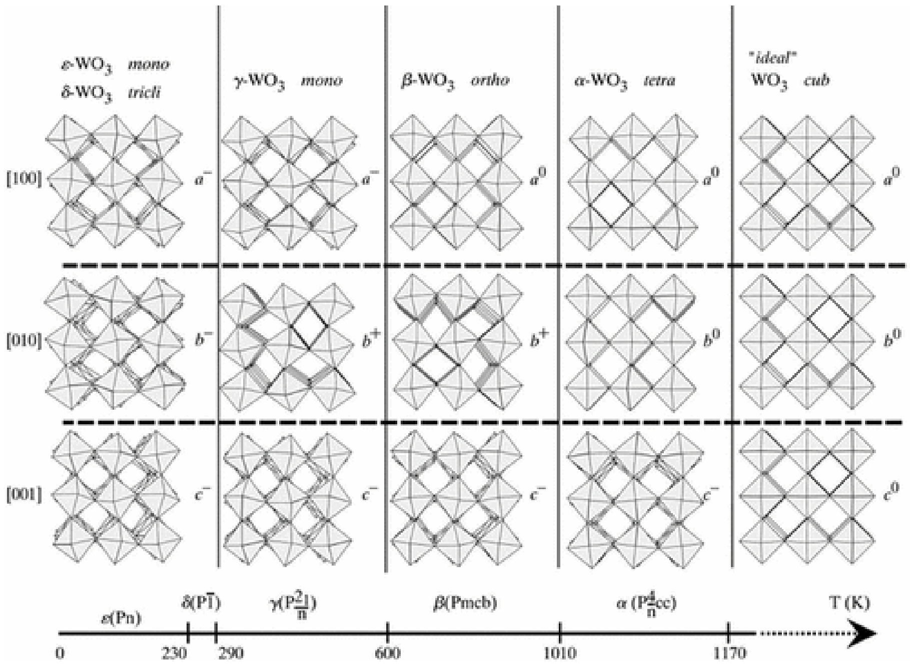


***Figure 1:*** *$WO_3$ structures shown with different millers index and various temperatures. [1]*

As shown in the *figure 1* the structure $WO_3$ decides to take is dependent on the temperature when the tungsten oxide is in a larger mass. The exact numbers are monoclinic II (ε-$WO_3$, <−43 °C) , triclinic ($\delta$-$WO_3$, −43 °C to 17 °C) , monoclinic I ($\gamma$-$WO_3$, 17 °C to 330 °C), orthorhombic ($\beta$-$WO_3$, 330 °C to 740 °C), tetragonal ($\alpha$-$WO_3$, >740 °C). In the real world the most common structures are $\gamma$-$WO_3$ and

$\delta$-$WO_3$ because of that their structures are relevant to the temperature on earth. Therefore the likes of $\beta$-$WO_3$, $\alpha$-$WO_3$ and $\varepsilon$-$WO_3$ is usually something that you find in a laboratory. All of the phases that have been mentioned are reversible which means that they commute between each other. Another phase of $WO_3$ that has not been mentioned before in the assignment is hexagonal (h-$WO_3$). h-$WO_3$ is also obtained from octahedral WO6 but it separates from the rest because it uses the form of three and six membered rings. The Hexagonal phase is a metastable phase and when it heats up to over 400 C it transforms to the monolinc state. [1][2]

There are also structures of WOx that are nonstoichiometric such as W20O58, W18O49 and W24O68. These are nonstoichiometric because of that the lattice is able to withstand a large amount of oxygen deficiency. The WOx that is nonstoichiometric is created by sharing the corners of WO6. When $x \to 3$ in WOx the shear planes are seen as expanded defects which leads to the structure being more stable. When the x value is going downwards the shear planes often interact and line up parallel. This leads to a more unstable structure. A rule is that if $x <= 2.87$ the structure is considered unstable. Another thing that changes depending on the x value is the visual of the substance. For example $x=3$ gives a yellow substance, $2<x<3$ gives a green and $x=2$ gives blue. The reasoning behind this is an additional broad absorption peak. [1][2]

# 3 Properties

The properties of a material is partly what gives the material its unique character. There are many different relevant properties that can be explored of a specific material. But in this case the following Thermal, Optical and Electrical properties have been decided to be explored.

## 3.1 Thermal

Thermal properties are how the substance behaves thermally. For ceramics in general the thermal properties are determined by bonding, structure, defects and so on. For tungsten oxide there is a known relation between the Seebeck coefficient and temperature.

The voltage gradient and the temperature difference is something that is relevant to the thermoelectric effect. The conversion of a voltage gradient dissimilar to the temperature. The thermoelectric effect of Tungsten oxide is something that is yet to be massively explored and has room for improvement on the research. The thing used for the thermoelectricity is the thermochromism of $WO_3$. Thermoelectric effect is something that is a thing for $Wo_3$ hydrates and stoichiometric. Something that affects the hydrates is the Seebeck coefficient. The seebeck coefficient (S) is measured in $VK^{-1}$. The Seeback coefficient is something that is used to calculate the magnitude of a thermoelectric voltage. This is created by a temperature difference in the material. The Seeback coefficient can be calculated in multiple ways and is something that is relevant to semiconductors as Tungsten oxide. The Seeback coefficient for the hydrates is approximately linear between temperature below zero to fifty degrees celsius but after that in the span of fifty to one hundred degrees it increases rapidly before decreasing exponentially. The Seeback coefficient is something that differentiate for which type of WOx you have. For example there is a linear relationship between the different types of $Wo_{2.95}$ and 2.9 meanwhile there is no relationship at all between $WO_{2.83}$ and $WO_{2.72}$. The highest Seeback constant for specially $WO_3$ is $600\mu VK^{-1}$at the given temperature two hundred degrees celsius. [3][1]

## 3.2 Optical

Tungsten oxide is something that can occur in multiple colors. The Optical property of tungsten oxide is probably what makes it the most unique and usable. The ability to change color is something essential to many of the different devices it is used in.

The bandgap is something that is essential to the Optical properties. The bandgap defines the absorption threshold which defines the visible region of Tungsten Oxide. The bandgap is the least amount of energy required for an electron to go from the valence state to the lowest state in conductors and semiconductors. For Tungsten oxide the bandgap is in the range of 2.6-3.25 eV. This specific band gap gives the blue color compared to its bulk form. Stoichiometric Tungsten oxide is transparent for most wavelengths. In some cases where the bandgap sizes samples are smaller it can give a yellow color. When the Bandgap is exceed by the photon energy the following equation applies

$$\varepsilon\alpha \propto (\varepsilon - E_g)^{\eta} \qquad \text{(Equation 1)}$$

Where $\alpha$ is the light absorption, $\varepsilon$ is the photon energy, $E_g$ is the Bandgap energy and $\eta$ is equal to 2. *Equation 1* shows that the light absorption and the photon energy is proportional to the photon energy , Bandgap and a constant. The nonstoichiometric Tungsten oxide as mentioned before is light green. The light green color is caused by a additional absorption peak that happens because of a electron transfer from $W^{6+} \rightarrow W^{5+}$. This phenomena gives a broad absorption in the span of the Blue-Green spectrum. A parameter that is essential to knowing when constructing optical devices is the refractive index of $WO_3$ that has the scale 2-2.5.
[1][8][12]

One of Tungsten oxides' most usable assets is that it can change color in its physical form. The tungsten oxide can go from optical clear to dark blue. There are two different ways for this to happen. Reducing gasses which is called gasochromic and applying voltage which gives electrochromism. There is also another type of reaction that is being studied which includes light or heat included chromic effects. The equation for the electrochemical reaction is further discussed down below under the "Electrochromic Device" header. [1]

## 3.3 Electrical

The Electrical properties of tungsten oxide is as big a deal as the optical and thermal properties. The electrical properties differ very much from metals and ceramics.

Semiconductors for metal oxides electrical conduction are heavily dependent on the concentration of electrons that move freely in their conduction band. The conduction band is the different energy levels that lead to the electrons moving freely. The concentration of the stoichiometric defects is the main thing that impacts the free electron concentration. Stoichiometry is something that also affects the electrical conductivity in the crystal. In the case of tungsten oxide it is a span of 10 to $10^{-4}$ S/cm. There are also plenty of other aspects that affect the conductivity. Phenomena as specific phase, film thickness , dopants , grain size and grain boundary. Because of that the conductivity is so dependent on so many different factors it is very hard to understand how much each factor affects the conductivity. A certain conclusion from this is that the electrical conductivity is very based on growth conditions and synthesis techniques. [1][9]

# 4 Applications

Tungsten oxide's properties give it a wide berth of areas that it is applicable for. This section covers some of the areas where most progress has been shown. Among them are electrochromic devices, pH-sensing, gas sensors, as well as photocatalysis and its uses.

## 4.1 Electrochromic devices

Electrochromism is the event of when a substance modifies its optical properties in a reversible manner when exposed to an external potential. This effect can be used for applications that need the ability to dynamically regulate the transmittance, reflectance, absorptance and emittance of the material [7][6]. The electrochromic properties of amorphous $WO_3$ is based on the intercalation of small cations ($H^+$, $Na^+$, or $Li^+$) into its lattice, which changes the material color from transparent to blue [6].

$$(WO_3 + H^+ + e^-)_{bleached} \rightarrow (xWO_3)_{colored} \qquad \text{(Reaction 2)}$$

An example of an application for an electrochromic device is "smart windows" which can change its color to reduce incoming light. This window can replace the function of regular window blinds. It is also widely used in certain types of displays and rear view mirrors for cars. [4] *Figure 2* shows a schematic layered structure of an electrochromic device used in the Boeing 787 Dreamliner airplane.

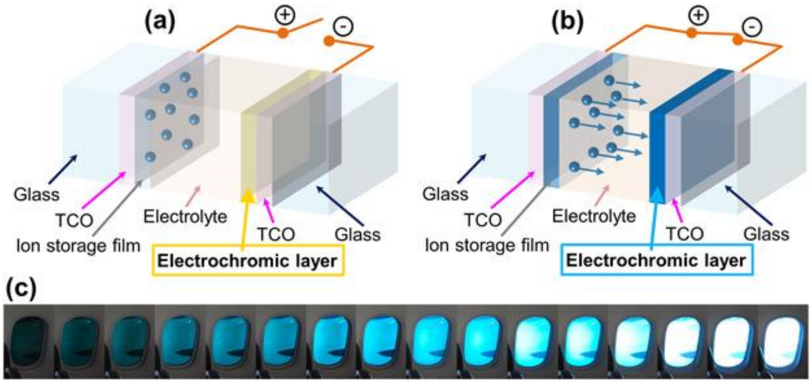


***Figure 2:*** *Schematic layered drawing of the smart window used in Boeing 787 Dreamliner airplane (a) transparent (b) colored [6].*

The outer layer is usually a glass material, but it can also be plastics. Following the glasspane is the TCO (transparent conductive oxide). The most common material used as a TCO is Sn-doped $In_2O_3$. Doping with other materials such as Zn and Nb also shows great electrical properties. However due to the cost of Indium caused by its scarcity other materials are also studied. In between the two TCO layers is a three layer construction consisting of two $WO_3$ thin films with an electrolyte separating them. When applying a small differential difference (<5 V DC) in the TCO, cations are injected in the $WO_3$ layer and the color changes towards dark blue (*reaction 2*). Reversibly, when applying a reverse potential bleaching occurs and the material becomes transparent again. [6]

## 4.2 pH-Sensing

One of the earliest features of tungsten oxide that was discovered and examined was its pH sensitivity. The sensitivity is based on hydrogen ions intercalating into the tungsten oxides $ReO_3$-type structure. Intercalation can be described as the shifting of an ion or a molecule injection into a layered structure, in this case the $ReO_3$-type structure which is also known as a defect perovskite because of its $ABX_3$-structure. Where the hydrogen ion is in the A-slot and $WO_3$ in the B- and X-slot, as can be seen in *Figure 3* below. The same chemical reaction as for the electrochromic effect (*reaction 2*), the intercalation of hydrogen ions results in the creation of tungsten bronze.

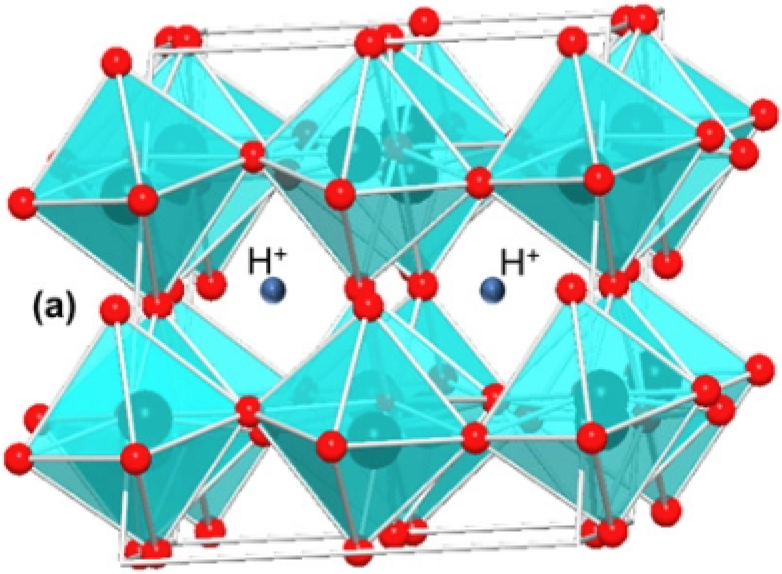


***Figure 3.*** *3D-demonstration of the monoclinic γ-WO3 interstitial intercalation of the hydrogen ions which is responsible for the materials pH sensing abilities [6]*

The pH detection method is based on the concurrent entry of both cations and electrons into the $WO_3$-structure, with the ensuing $H_xWO_3$ phase having a greater electric conductivity than $WO_3$. To then calculate the relationship between the electrode potential and the pH value, the Nernst equation is used.

$$E = E^0 - \frac{RT}{zF}\ln Q \qquad \text{(Equation 2)}$$

Where $E$ represents the measured potential, $E^0$ represents the standard potential, $R$ represents the universal gas constant (8.314J/Kmol) , $T$ represents the temperature (K), $z$ represents the number of electrons that are transported in the process, and $F$ is the Faraday constant(96485.34C/mol)

The application of this property in $WO_3$ has been largely observed in the development of pH sensors. For instance, different methods of constructing miniaturized electrodes that have tungsten nanowires as their basis have been used. For example, it was made possible to measure pH in very small amounts, down to nanoliters with the help of nano-electrodes. Micro-electrodes were used to measure the pH values inside bubbles and cavities. [6]

## 4.3 Gas sensors

In recent years the use of tungsten oxide has been on the forefront of semiconductors when it comes to thin film technology of gas sensors. The technology is mostly used for monitoring air quality or detecting potentially damaging gasses. The gas sensors that are using metal oxide semiconductors (MOS) as their sensing layer have been particularly popular in the research field due to their formidable sensitivity, modest size and relatively low cost. The areas in which MOS gas sensors can be used are still yet determined but some indications show great promise in sections such as smart homes, biomedicine and wearable devices to name a few.

What sets tungsten oxide apart from other patterned band gap semiconductors is its valuable electrochromic, photochromic and gasochromic properties. $WO_3$ gas sensors have already been used to detect a variety of harmful and dangerous chemicals that includes gasses such as nitrogen dioxide ($NO_2$), ammonia ($NH_3$) and hydrogen sulfide ($H_2S$) to name a few.

The main mechanism of a resistive type metal oxide semiconductor gas sensor is that the resistance fluctuates when the gas concentration changes. The resistance of the metal oxide may alter while exposed to the analysis gas, depending on the different types of charge carriers and surface responses to the gas.

The fundamental idea of $WO_3$-based gas sensors is about the same as other resistive-type sensors, which was stated above, where the variation in resistance conveys information regarding the target gas, such as its type and concentration. $WO_3$ is a typical n-type semiconductor, where the electrons serve as the primary charge carrier. When exposed to a reductive gas, resistance decreases whereas resistance increases when exposed to an oxidative gas. [5]

## 4.4 Photocatalysis

One of the most promising strategies to solve the ongoing environmental and energy problems is with the help of solar driven photocatalysis and photochemical reactions. Generally photocatalytic activity is achieved by illuminating a semiconducting material, while submerged in a solvent, to photons that have an energy level larger or equal to the semiconductors' band gap. As a result, electron hole pairs are formed in the material, which generates free radicals which can produce further reactions [1].

As $WO_{x\leq3}$ has a bandgap between 2.6 to 3.25 eV, due to its stoichiometric properties and morphology, it is one of the most studied n-type photocatalysts for water oxidation, water splitting, and $CO_2$ reduction [2]. However, compared to other semiconductor materials $WO_{x\leq3}$ suffers in areas such as slow charge transfer and rapid electron hole recombination, but its advantage is its exceptional stability in acidic environments [1][2].

Following, four photocatalysis usages for $WO_3$ will be discussed as follows.

### 4.4.1 Water oxidation

Water oxidation is the central reaction of natural photosynthesis. Although the exact reaction of "unnatural" water oxidation differs slightly from natural photosynthesis, the general reaction of water splitting is as follows.

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2 \qquad \text{(Reaction 3)}$$

The criteria for a material to be used as an photocatalyst is that the valence band level is more positive than the standard redox potential of $H_2O/O_2$ (1.23 eV). The valence band level of $WO_{x\leq3}$ is located at around 3.0 eV which makes it promising for water oxidation. Recent decades of development in the field of WO systems has enabled the systems to outperform the activity of the natural system [10]. Water oxidation is an important step which provides the necessary electrons for proton reduction that is essential for both $CO_2$ reduction and water splitting [2].

### 4.4.2 Water splitting

Water splitting is the reaction that breaks down oxygen and hydrogen from water (*reaction 4*).

$$2H_2O \rightarrow 2H_2 + O_2 \qquad \text{(Reaction 4)}$$

Water splitting when using only one single photocatalyst is attained when the water's potential is +0 to +1.23 eV and the range of the band gap straddles the standard reduction. However $WO_{x\leq3}$ does not achieve this criteria and thus cannot be used as a one-step photocatalyst. However, by introducing another $H_2$ photocatalyst to create a two-step excitation system is an alternative. In these situations the $WO_{x\leq3}$ still functions as an $O_2$ evolution material [2]. A two-step water splitting system can be composed, as demonstrated by Tang et. al, by using $g\text{-}C_3N_4$ (Graphitic carbon nitrides) and $WO_3$ with $I^-/IO_3^-$ (Iodate) as a redox mediator, which yields in $H_2$ and $O_2$ from water under visible light [11].

### 4.4.3 $CO_2$ reduction

$CO_2$ reduction through photocatalysis with $H_2O$ is an endothermic reaction when turned into hydrocarbon fuels, such as HCOOH, CH4, HCHO, and $CH_3OH$. Two of the reactions are as follows.

$$CO_2 + 2H_2O \rightarrow CH_3OH + 3/2O_2 \qquad \text{(Reaction 5)}$$

$$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2 \qquad \text{(Reaction 6)}$$

Where *reaction 5* has the gibbs free energy of $\Delta G^{o}$ = 702.2 kJ/mol and *reaction 6* has $\Delta G^{o}$ = 702.2 kJ/mol. The basic principle is that molecules are adsorbed on the catalyst ($WO_3$) surface which triggers a row of chemical reactions that will cleave the C-O bonds and form C-H bonds which eventually produces hydrocarbon fuels. [2]

### 4.4.4 Degradation of organic compounds

Due to the electrons and vacancies that emerge during photocatalysis with $WO_3$ it can react with adsorbed $O_2$ and $OH^-$ in its surroundings. Since the conduction band of $WO_3$ has a slightly higher reduction potential than of an $H_2/H_2O$ reaction and that its valence band potential is substantially greater than the $H_2O/O_2$ reaction's oxidation potential, it enables photocatalytic oxidation degradation of $WO_3$ for many organic compounds. This reaction enables the $WO_3$ to function as a reactive oxygen type material that can mineralize pollutants. In addition, thanks to the great stability in acidic environments it has a promising use for wastewater treatment for water that contains organic acids [2][12].

# 5 Conclusion

In this report we summarized a large sample of scientific reports regarding tungsten oxides. Our main focus has been on its structures, properties and applications.

There are many different ways to produce Tungsten oxide and for the solution $WO_{2.72}$ the main processes are chemical vapor transport, solid phase reaction, hydrothermal and solvothermal processing. Every one of these comes both with their upsides and downsides. The most commonly found structures are $\gamma$-$WO_3$ and $\delta$-$WO_3$ because of that their structures are relevant to the temperature on earth, but many more structures are found in labs and are used for experiments.

The reason that makes tungsten oxides so useful is thanks to its unique properties that makes them an important group of materials for energy, photo and optic related applications. Many breakthroughs have recently been made in various areas of the oxides which has allowed it to become highly efficient for water splitting, $CO_2$ reduction and degradation of organic materials. The existence of highly tunable oxygen vacancies in $WO_{x \leq 3}$ is one of these breakthroughs and this unique benefit that allows for fascinating new applications, but also gives the opportunity to improve the efficiency of current applications.

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