Recent Progress in the Synthesis and Potential Applications of Two-Dimensional Tungsten (Sub)oxides

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Abstract: While WO$_3$ is one of the most studied metal-oxides in bulk, it is increasingly gaining interest as a two-dimensional (2D) material as it exhibits different behaviour compared to bulk. In addition, many substoichiometric WO$_{3-x}$ ($0 \leq x \leq 1$) phases exist both in bulk and 2D form. These Magneli phases have different physical and chemical properties than their WO$_3$ counterparts. By introducing oxygen vacancies, the physical and chemical properties of 2D tungsten (sub)oxide nanomaterials can be further altered. This review focuses on synthesis pathways of 2D tungsten (sub)oxides reported so far, and their subsequent use for various applications. The different stoichiometries and additional oxygen vacancies that appear in these materials, combined with their low thickness and high surface area, make them interesting candidates for gas sensing, catalytic application or in electronic devices.

Keywords: two-dimensional materials · metal oxides · tungsten suboxides · synthesis · applications

1. Introduction

Tungsten (VI) oxide (WO$_3$) is one of the most investigated transition metal oxides due to various potential applications, such as in photochromic smart windows,[1] in optoelectronics,[2] gas sensing and photocatalysis,[3] as supercapacitors,[4] as nanostructured thermoelectrics,[5] etc. The WO$_3$ forms a rich variety of crystal structures composed of corner-sharing WO$_6$ octahedra, which differ in tilting angles, displacements of the W cation from the centre of the octahedron, and rotation of WO$_6$ octahedra with respect to ideal cubic (ReO$_3$ type) structure.[5] In bulk, partially reversible inter-phase transformations occur upon heating in addition to the formation of a metastable phase.[6] At nanoscale, phase transitions occur at temperatures lower than in bulk and depend mostly on the size of WO$_3$ nanoparticles.[7]

Recently, two-dimensional (2D) nanostructures, including 2D-WO$_3$, have attracted a lot of attention among researchers due to their novel physical and chemical properties, which differ from their bulk counterparts.[8] High surface area, appearance of crystalline planes/surfaces that are not available in bulk materials, and stability of crystal phases declared as metastable in bulk systems are just some of the examples. Due to their low-dimensional nature, quantum confinement effects come into play, changing their electronic properties. This is providing a great opportunity for their use as components in novel sensors, energy conversion devices, transistors, to name a few. Different particular particle shapes, such as pseudospherical nanometre-sized particles, nanowires, nano-discs and flakes, were already synthesized with various growth techniques.[9]

Besides the stoichiometric WO$_3$, many substoichiometric WO$_{3-x}$ phases exist, where $0 \leq x \leq 1$. The electrical, optical, and structural properties of tungsten suboxides depend strongly on the degree of reduction (i.e. x) and consequently differ from stoichiometric WO$_3$.[10] Moreover, for additional tuning of their properties, oxygen vacancies can be induced in WO$_3$ or WO$_{3-x}$. The abundance of tungsten ore in combination with the low-dimensional nature, a wide range of substoichiometric phases that can be further altered by inducing oxygen vacancies, 2D tungsten (sub)oxides offer a platform with diverse and tuneable properties for a great variety of applications.

This review focuses on current synthesis approaches to obtaining 2D tungsten (sub)oxide materials. In addition, the progress in their utilization in various applications, such as gas sensing, catalysis and photodetection, is discussed in terms of current state of the art and future outlook.

2. Synthesis, Morphology and Structure

One of the first 2D-WO$_3$ crystals was prepared more than 15 years ago, when monoclinic WO$_3$ nanosheets were synthesized by a solvothermal reaction.[11] The square nanosheets were 150 nm in size and thin enough for a direct HR TEM
analysis. In the following years, different methods of synthesis were reported. The 2D-WO$_3$ nanoparticles were crystallized in the monoclinic WO$_3$ phase via wet chemical synthesis\[^{12}\] topochemical conversion,\[^{13}\] hydrothermal,\[^{8}\] solvothermal,\[^{14}\] exfoliation and oxidation of WS$_2$\[^{15}\] and microwave irradiation,\[^{16}\] to name a few. The morphologies of synthesized nanoparticles range from rectangular nanoflakes,\[^{13}\] irregularly shaped nanodisks,\[^{13}\] leaf-like nanoplatelets,\[^{17}\] and nanoflakes,\[^{18}\] with the sizes ranging from 20 nm to 500 nm in lateral dimensions and from 5 nm to 60 nm in thickness. An example of a nanoplate is shown in Figure 1 a, b).

Although at room temperature only the monoclinic WO$_3$ phase is stable in bulk, other crystal structures were stabilized in form of 2D-WO$_3$ phase is stable in bulk, other crystal structures were stabilized. Hexagonal WO$_3$ nanosheets were synthesized from the colloidal suspension of BaWO$_4$-PAA\[^{19}\] orthorhombic WO$_3$ nanoflakes were synthesized using sodium tungsten Na$_3$WO$_4$$^*$$^*$$^*$$^*$H$_2$O as precursor by a simple free template precipitation method,\[^{20}\] triclinic WO$_3$ nanoparticles were synthesized through a hydrothermal route,\[^{21}\] and cubic WO$_3$ nanosheets were synthesized by direct reduction.\[^{22}\] Novel octahedral molecular sieves (h'-WO$_3$) with the diameter between 20 and 80 nm and thickness of 3–10 nm were also synthesized and are shown in Figure 1 c).\[^{23}\]

With various synthesis methods, different crystal facets could be exposed, which are not available in bulk materials. It was reported that (100), (010), and (001) facets could be exposed with the use of different surfactants,\[^{12,24}\] solvents,\[^{21}\] specific precursors,\[^{13,25}\] or the synthesis method. Their atomic structure and electronic properties differ due to the nature of the crystal structure, and thus play an important part in the physical and chemical properties of the material.\[^{26}\] For example, it was reported that (100) facets show higher evolution rate of O$_2$ in water splitting than WO$_3$ without a preferred crystal face.\[^{26b}\]

As stated in the Introduction, the stoichiometric WO$_3$ can also be reduced into substoichiometric WO$_{3-x}$ using different techniques such as chemical vapor transport (CVT),\[^{27}\] heating under controlled atmosphere,\[^{28}\] and electron beam irradiation in a TEM microscope.\[^{28b,29}\] The substoichiometric WO$_{3-x}$ can be synthesized with a wide variety of hydrothermal and solvothermal methods,\[^{30}\] layer deposition methods, such as atomic layer deposition (ALD) and chemical vapour deposition (CVD).\[^{31}\] These suboxides grow in different structures such as films,\[^{32}\] needles,\[^{33}\] nanowires,\[^{27}\] nanorods,\[^{34}\] and nanodots\[^{35}\] and can crystallize in similar structures as tungsten bronzes with a general formula A$_x$WO$_3$ where A is an electropositive element.\[^{36}\] While in the tungsten bronzes W$_5$$^+$

Figure 1. a) Low-magnification and b) high magnification TEM images of WO$_3$ nanoplates (Reprinted from reference [13] with permission from John Wiley and Sons); c) HAADF-STEM micrograph of a h'-WO$_3$ framework. The inset shows the arrangement of tungsten octahedra (Reprinted from reference [23] with permission from Springer Nature); d) HRTEM image of a cross-section lamella showing semi-regularly distributed CS planes in a W$_{52}$O$_{101}$ tungsten suboxide. The arrow points to a defect (Reprinted from reference [10] with permission from the Royal Society of Chemistry.)
state appears due to the presence of the electropositive element, in WO$_{3-x}$ it occurs through the intrinsic oxygen vacancies. It has been shown that even when $x$ in WO$_{3-x}$ is less than 0.0001, the oxygen atoms are not removed randomly but form ordered structures.$^{[38a]}$ Within the material, crystallographic shear (CS) planes, pentagonal columns (PC), and oxygen vacancy walls (OVW) are formed to accommodate the oxygen vacancies, as shown in Figure 2.

The term crystallographic shear comes from the shearing of two adjacent blocks of WO$_3$. In a CS plane, corner sharing WO$_6$ octahedra that are a part of the CS plane become edge sharing WO$_6$ octahedra.$^{[38]}$ While a single CS plane is considered a defect, an array of equally spaced CS planes forms a WO$_{3-x}$ crystal with a defined stoichiometry. The CS planes can be described in terms of \{hkl\} planes of WO$_3$, which crystallize in the ReO$_3$ type structure.$^{[39]}$ For $x < 0.007$, the \{102\}$r$ CS planes are randomly distributed.$^{[28d]}$ The increase of the degree of reduction (i.e. increasing $x$) increases the density of CS planes, resulting in a formation of their ordered arrays, which form the W$_x$O$_{3n-1}$ tungsten suboxides. When $x$ approaches 0.1, the formation of \{103\}$r$ CS planes become favourable over the formation of \{102\}$r$ CS planes, forming the W$_x$O$_{3n-2}$ tungsten suboxides. While CS planes are observed in less reduced WO$_{3-x}$ ($x \leq 0.2$), PC structures form only in more reduced WO$_{3-x}$ ($x \geq 0.2$). The PC are periodic structures of WO$_3$ bipyramids that share their equatorial edges with WO$_6$ octahedra.$^{[40]}$ Within structures with PC, three-, four-, five- and six-sided tunnels can also form as in the case of W$_{18}$O$_{49}$ or W$_{60}$O$_{14}$.$^{[27,44]}$ Although OVW were proposed as the precursors of CS planes, there are very few articles where these were experimentally observed.$^{[42]}$ The abundance of CS planes and PCs largely depends on the degree of reduction.

With sufficiently low reduction, single oxygen vacancies can be produced.$^{[43]}$ In this case, oxygen atoms are removed from the surface, forming oxygen vacancies. To minimize the surface energy, single PCs appear on the surface, stabilizing the structure. Although technically oxygen vacancies reduce WO$_3$ into WO$_{3-x}$, in the majority of the materials reported in the literature, it is not clear what kind of structure formed within the material. Thus, the term substoichiometric tungsten oxides (WO$_{3-x}$) is used interchangeably in literature for materials with ordered CS and PC structures, as well as for materials with induced oxygen vacancies.

For 2D-WO$_{3-x}$ materials, different stoichiometries were identified, such as W$_{18}$O$_{49}$ and W$_{60}$O$_{14}$ nanosheets,$^{[45]}$ as well as materials with mixed stoichiometry,$^{[46]}$ multi-stoichiometric nanoplates,$^{[47]}$ and nanomaterials with unknown stoichiometries.$^{[48]}$ Similarly to 2D nanoparticles, 2D-WO$_3$ and 2D-WO$_{3-x}$ thin films can be made using atomic layer deposition,$^{[39a]}$ molecular beam epitaxy,$^{[48]}$ and vapor-phase deposition.$^{[18b]}$ Different stoichiometries can be prepared, from monoclinic WO$_3$,$^{[31a]}$ to W$_{18}$O$_{49}$,$^{[49]}$ and WO$_2$O$_{2n}$ bilayer structure,$^{[18b]}$ with the thickness ranging from a monolayer up to several tens of nm. Owing to the large area of deposited films, they can be used in many applications such as electrochromic displays, solar cells, and supercapacitors.$^{[50]}$ Due to the formation of CS planes, as shown in Figure 1d), the electronic and optical properties differ from monoclinic WO$_3$ and they may have an advantage in applications such as water splitting,$^{[37,51]}$ near-infrared shielding,$^{[44]}$ as anode materials for high-performance Li-ion batteries,$^{[52]}$ photocatalysis,$^{[53]}$ and in domain boundary engineering.$^{[54]}$

Although the majority of the reported stoichiometries were determined from XRD measurements, it is not the most suitable and precise method to use in the case of tungsten suboxides, as the differences between phases are too small to be detected.$^{[39]}$ Only for highly crystalline samples, where the diffraction peaks from the low index (hkl) planes are observed, can the stoichiometry be determined by using XRD as the main tool. HRTEM images and electron diffraction patterns can be used to further elucidate the true crystal structure of tungsten (sub)oxides.

A short summary of the synthesis methods, particle sizes, crystal structures, exposed faces, and applications of 2D-WO$_3$ and 2D-WO$_{3-x}$ is presented in Table 1.

### 3. 2D-WO$_{3-x}$ for Applications

Among the biggest advantages of the 2D morphology are the large specific surface area, increased number of active sites and confined thickness, which make these nanostructures promising candidates for gas sensing, catalytic applications and electronic or photonic devices. Additionally, the 2D-WO$_3$ and 2D-WO$_{3-x}$ are interesting from the aspect of defect engineering, where finding the optimal concentration of oxygen vacancies could lead to fine bandgap tuning, increased amount of charge carriers and photocurrents, whilst maintaining the crystallinity. Nevertheless, ultrathin WO$_{3-x}$ nanosheets have not been sufficiently studied in terms of applications, despite their substantial amount of reactive (002) crystal facets and a high specific surface area.

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**Figure 2.** Crystal structures of some stoichiometric and sub-stoichiometric tungsten oxides. Reprinted with permission from reference [37]. Copyright 2021 American Chemical Society.
Materials preferred in gas sensing applications tend to have a good adsorption-desorption mechanism and a pore-rich morphology. This makes 2D-WO$_3$ and 2D-WO$_{3-x}$ promising candidates, since the oxygen vacancies play an important role in adsorption-desorption phenomena. In order to obtain the enhanced gas-sensing performances, morphology and surface design are required. Other important parameters for optimisation of sensor performance are sensitivity, stability, selectivity, adsorption and desorption ability, crystal structure, electronic and chemical properties etc. In addition, since these reactions rely closely on the interaction of the surface of the material and the target molecules, the performance depends strongly on the exposed facets and surface area. Different facets of the same structure can have different dangling bonds and electronic structure, exhibiting different physical and chemical properties. As seen in Section 2, tuning the synthesis can expose selected facets, with which the gas sensing ability can be optimized. When it comes to gas sensing capabilities of metal oxides, they are mostly based on the oxidation-reduction reaction of the detected gases. As the oxidation-reduction reaction takes place on the surface, the physical and chemical properties of the facets play an important role. If the planes are terminated with positive ions, they are able to adsorb the oxygen species and target molecules due to unsaturated oxygen coordination, improving gas sensing capabilities. It was shown that for the monoclinic WO$_3$, (002) crystal facets exhibit enhanced photocatalytic CO$_2$ reduction and photoelectrochemical (PEC) water splitting capabilities compared to (200) and (020) facets, due to improved photoinduced charge carrier separation efficiency. Another important factor for gas sensing is selectivity. The sensor has to be able to discriminate the selected gas in a mixture of gases, and this is determined by the adsorption and subsequent chemical oxidation on the surface of the potential sensor material. The sensitivity is largely affected by geometrical and chemical heterogeneities of the reacting surface. Materials with higher amount of surface defects, where adsorption and catalytic reaction may take place, are preferred.

Reducing NO$_2$ emissions is an important task, as very low concentrations (1 ppm) can induce respiratory issues. Since NO$_2$ sensors should operate in the ambient oxygen environment, materials under consideration need to have good air durability, as well as high selectivity and sensitivity, fast response and recovery time. 150 nm thick WO$_3$ films were shown to be good candidates for NO$_2$ sensing. Here, Cantalini et al. showed that the sensor sensitivity increases with the increase in surface defects concentration, while the long-term stability depends on the optimization of the annealing process of the films. In this case, the films were more stable when annealed for longer times, which stabilizes the surface defects. In a different study, 10 nm thick WO$_{3-x}$ nanosheets showed high sensitivity and selectivity to NO$_2$. The best performance was obtained at 50 ppb NO$_2$ at 140°C with response and recovery times of 140 s and 75 s, respectively. With a further reduced thickness, Khan et al. made physiosorption-based NO$_2$ sensors from 4 nm thick substoichiometric WO$_{3-x}$ nanosheets. The optimal operating temperature for samples annealed at different temperatures was 150°C. This temperature is significantly lower than for the conventional chemisorptive metal oxide gas sensors, which operate above 200°C. As the operating temperature increased, the response decreased. In this regime, the rate of adsorption is lower than the rate of desorption. The best responsivity (here, the input/output ratio of the electrical resistance) to 40 ppb was reported to be 30, which is more than an order of magnitude higher than for the nanocrystals. This work furthermore empha-
sizes the influence of the stoichiometry on performance and properties. These materials were tested in the NO₂ concentration range of 20 to 2000 ppb, but the sample annealed at 225°C was overly sensitive, reaching saturation beyond 120 ppb. The saturation occurs because as the concentration of the NO₂ increases, these surface-adsorbed molecules act as acceptors available to take electrons from the suboxide and at a certain concentration, there are no electrons left. The sample annealed at 225°C has the WO₃₋₀.₉₆ stoichiometry, which is known to be semiconducting, while the unannealed and annealed at 450°C have the WO₂₋₃ stoichiometry that is more metallic and requires more electron transfer for full off/on switching. Therefore, the changes in crystal structure and stoichiometry can result in different performance of sensors. The same samples were studied for NH₃, H₂S, CO₂, H₂ and humidity sensing, but showed far less promise. This is explained with greater molecule-surface binding energies for NO₂ and WO₃.

In another study, WO₃ nanosheets prepared by microwave irradiation method showed promise as humidity sensors. With the relative humidity working range of 10–90%, the maximum sensitivity was estimated to be 98%, with the response and recovery time of 25 and 15 s, respectively. They showed high stability, with only a 3% drop in performance after three months, making them suitable candidates for high performance sensing.

Ultrathin (5 nm) WO₃ sheets were successfully used as gas sensing material for the detection of xylene, a volatile organic compound that has adverse effects on human health. The sensing mechanism can be explained as follows: oxygen molecules from air get adsorbed on the surface of WO₃ and get chemisorbed into O²⁻, O⁻ or O₂⁻ by capturing electrons from the material’s conduction band. Upon xylene introduction, it reacts with these species, releasing the trapped electrons. In the case of thin sheets, these charge layers may cover the entire surface, increasing the material’s sensitivity. This sensing mechanism is depicted in Figure 3 a).

2D-WO₃ nanoplatelets with 10–50 nm thickness were used as hydrogen sensors. The most efficient interaction of WO₃ with the molecules that contain hydrogen atoms is through intercalation. The intercalated H⁺ ions embed themselves into WO₃ lattice, and the electrons released from the lattice are transferred to the lowest unoccupied energy levels. This in turn changes the band structure of the metal oxide and increases the conductivity, which can be used for sensing applications. The mechanism of H₂ sensing is based on the changes in electrical conductance, which strongly depends on the content of oxygen vacancies and H⁺ ions. The oxygen adsorbing capabilities in turn depend on the surface area of the material, morphology and the operating temperature. As the oxygen species adsorbed on the surface capture electrons from the material, the hole concentration increases, forming an electron-depleted layer at the surface of the platelets.

Triclinic WO₃ nanosheets with 35 nm thickness were synthesized in a process that enables the control of the exposed facets. These nanosheets were used as l-butylamine sensors, and the sheets with the exposed (010) facets demonstrated the best performance. It was shown that (001) and (100) facets have more O-terminated planes, while (010) have more W-terminated planes.

As n-type semiconductors, WOₓ₋₄ materials are good candidates for ethanol sensing. When the platelets are exposed to air, the ethanol molecules from the atmosphere can get adsorbed on the surface. They can subsequently capture electrons from the conduction band of WOₓ₋₄, forming adsorbed oxygen ions (O⁻, O₂⁻, O₂⁻), producing an electron-depletion layer on the surface. When the sensor gets exposed to ethanol, the ethanol molecules get chemisorbed on the surface and oxidized by the adsorbed oxygen ions. The oxidation promotes the return of the depleted electrons back to the conduction band, resulting in the decrease of the thickness of the electron-depletion layer. As a result, upon ethanol exposure, electrical current increases. The sensors of WO₃ nanoplatelets annealed at different temperatures were tested at the operating temperature of 300°C for various ethanol concentrations. It was shown that the sensitivity improved as the gas concentration increased. The gas sensor made of nanoplatelets with 500–1000 nm in lateral size and 50 nm thickness annealed at 450°C had the best alcohol sensing performance, due to the high crystallinity of the nanoplatelets.

The sensor maintained the initial response upon seven successive tests to 100 ppm of ethanol, showing good stability and reproducibility. The plate-like morphology and high crystallinity enable effective adsorption and rapid diffusion of the ethanol molecules. WO₃ platelets, produced by laser-assisted synthesis and with 70 nm thickness, were tested as ethanol sensors both in their pristine form and decorated with 8 nm Au nanoparticles. The pure platelet sensor reached the

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**Figure 3.** Schematic illustrations of the sensing mechanism of 2D-WO₃ towards a) xylene (Reprinted from reference [3], with permission from Elsevier) and b) acetone and ammonia (Reprinted from reference [24], with permission from Elsevier).
maximum response (current ratios through the sensor with and without the target gas) of 28 at 390 °C for 100 ppm of ethanol. With the added Au particles, the optimal temperature was lowered to 300 °C, with the 3.5-fold increase of the response value. The difference is attributed to the increased thickness of the electron-depletion layer, whereby Au nanoparticles accelerate the reaction between the ethanol molecules and adsorb oxygen ions.

Nanoplatelets of monoclinic WO$_3$ with 70–100 nm in lateral size and 30 nm of thickness were investigated as acetone and ammonia sensors due to their high crystallinity and smooth 2D surface. These nanoplatelets do not have oxygen vacancies, but an abundance of surface chemisorbed oxygen. Those properties make them excellent gas sensors towards acetone at 300 °C, with response and recovery times of 3 s and 7 s, respectively, at 10 ppm of acetone. Additionally, this sensor showed a wide response range (1–500 ppm), and stability. It was shown that active O$^-$ plays a leading sensing role for acetone. In the case of ammonia sensing, the optimal operating temperature was found to be 140 °C, with the response and recovery times of 39 s and 10 s, respectively; response region of 5–500 ppm and high selectivity. The sensing mechanism and the sensor response are shown in Figure 3 b).

### 3.2 Electrical Properties: Conductivity and 2D Photodetectors

The presence of the free electrons in the conduction band is the dominant factor in the electrical conductivity of these materials. These free electrons mainly come from CS planes, PC structures, oxygen vacancies, and other defects. Even in the case of a single crystal, the electrical conductivity can span five orders of magnitude ($10^{-4}$–10 S cm$^{-1}$), depending on the stoichiometry, with the charge carrier concentrations spanning the similar range ($10^7$–$10^{12}$ cm$^{-3}$). The amount of oxygen vacancies and the stoichiometry strongly depend on synthesis conditions and structural factors, which heavily influence the conductivity. This makes tungsten (sub)oxides interesting in terms of tailoring the material properties for specific electrical applications.

Bulk monoclinic WO$_3$ is a wide bandgap n-type semiconductor. The n-type semiconductor properties stem from oxygen vacancy-type defects. Bandgap corresponds to the difference between the top of the valence band (filled O 2p orbitals) and the bottom of the conduction band (empty W 5d orbitals), and is typically reported as 2.62 eV. Bulk, stoichiometric WO$_3$ is therefore transparent in the visible wavelength range. Another thing to consider when designing optical devices based on WO$_3$, is its large refractive index of up to 2.5. On the other hand, oxygen vacancies due to true, point-like defects in WO$_3$, are major contributors in the improved photocurrent density. In n-type metal oxides, these oxygen vacancies act as shallow donors. These electrons may fill the acceptor states below the conduction band minimum, making inter-bandgap states. If these shallow defect states remain unfilled, they can act as electron traps, resulting in the increased photodetector lifetimes. Due to the quantum confinement effects, 2D-WO$_3$ have a larger bandgap and more positive conduction and valence band edges. For nanostructured semiconductors, the bandgap generally increases with the decrease in size, resulting in the blueshift of the optical absorption band edge. It should be pointed out that the quantum confinement effect can occur in two different regimes. In the strong regime, the size of the material has to be much smaller than its Bohr radius, which is estimated as 3 nm for WO$_3$. The bandgap is significantly altered because the electron wavefunctions are perturbed directly. In the weak regime, when the crystallite size is larger than the Bohr radius, the bandgap energy changes are subtler, as the wavefunctions are indirectly perturbed. Therefore, the crystallite size plays an important role in bandgap engineering.

In bulk and in form of nanowires, WO$_3$ photodetectors showed a relatively slow response time and low on/off ratios. It is to be expected that 2D nanosheets have an improved performance.

50 nm layers thick WO$_3$ layers were deposited on a graphene back electrode (on a PET substrate), in order to engineer a transparent, flexible UV detector, as shown in Figure 4 a). These photodetectors were subsequently tested under 325 nm UV light or an alternating on and off UV source in 10 s intervals. The detector had a typical p-type Schottky contact barrier $I–V$ response. The time responses are highly stable and reproducible, with no degradation after tens of on-

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**Figure 4.** a) The fabricated flexible photodetector made of a WO$_3$ nanosheet on PET substrate (Reprinted from reference [74], with permission from Springer); b) The time-resolved photocurrent of the photodetector in response to light on/off at an irradiance of 131 mW cm$^{-2}$ with 365 nm light (Reprinted from reference [79], with permission from Elsevier); c) Spectroscopic responsel of the WO$_3$ nanobelt photodetector (shown in inset) measured at various wavelengths ranging from 250 to 700 nm at a bias of 1 mV (Reprinted with permission from reference [80]. Copyright (2015) American Chemical Society); d) Three-dimensional schematic view of the monolayer WO$_3$ photodetector and the focused laser beam used to probe the device. (Reprinted from reference [82], with permission from Elsevier).
off switching cycles. Interestingly, there was an increase in photocurrent with prolonged irradiation time, possibly due to its photochromic effect under UV radiation.\[74\] A 12 nm (approximately 16 molecular sheets) thick WO\(_3\) nanosheets photodetector, with two Cr/Au electrodes, was irradiated with a 365 nm monochromatic light.\[79\] This source was chosen as it is approximately at the position of the bandgap. The device exhibited a reversible on/off ratio of 2000, making it a high-quality photosensitive switch. The rise and the decay time were estimated to be 40 ms and 80 ms, respectively, which is much faster than that of the nanowires (20 s). The decay time was longer than the rise time, due to the presence of several recombination processes, such as surface and Auger recombination. Spectral responsivity, defined as the photocurrent generated per unit power of incident light on the effective area of a photodevice, was estimated as 293 AW\(^{-1}\). The time-resolved photocurrent in response to on/off light is shown in Figure 4b).

Additionally, polycrystalline WO\(_3\) 200–300 nm thick nanobelts were successfully used as a building block of a UV photodetector.\[90\] One individual belt consisted of dense nanoparticles of 20 nm in size. Using gold electrodes, this photodetector was assembled on a SiO\(_2\)/Si substrate and the photoresponse was recorded for the light excitation between 250 and 700 nm, as shown in Figure 4c), with the maximum sensitivity observed at 400 nm. The photoresponse has a slight drop for the wavelengths shorter than 400 nm, as explained by the enhanced absorption of the high-energy photons near the surface, while the increase in the longer wavelengths was attributed to the transition of the carriers from defect states to the conduction band.\[81\] P–I–V curves recorded in dark and under illumination are nonlinear, indicating Shottky contact between the sample and the electrodes. The photoexcited currents were much greater than dark currents, with a photo-dark current ratio of 1000. The superior performance compared to monocrystalline WO\(_3\) was attributed to the abundance of grains and boundaries that suppress the dark currents, and the increased photocurrent due to band-gap modulation.

Finally, a monolayer WO\(_3\), produced by atomic layer deposition on a SiO\(_2\)/Si wafer, as shown in in Figure 4d), was used for UV-A (315–400 nm) spectrum detection, which represents 95% of the UV radiation that reaches the Earth’s surface.\[82\] This detector was shown to have an extremely fast response time (<40 μs, 400 times faster than in the case of WO\(_3\) nanosheets\[79\]), stability of more than 200 cycles and photoresponsivity of 0.33 AW\(^{-1}\). This value is more than two orders of magnitude greater than for the previously reported WO\(_3\) photodetectors, with the reduced thickness as the most important factor for such an improvement in performance. Additionally, the photodetector was tested under 320 nm light for different bias and back-gate voltages. In the dark, with no bias, a depletion sub-layer near the surface of the monolayer is formed, as the surrounding O\(_2\) adsorbs on the material. With the applied bias, the current through the monolayer is low as the conductivity is low because of the depletion layer. When the device was put under the UV radiation, the photogenerated holes moved to the surface and desorbed the oxygen, in turn decreasing the width of the depletion sublayer and increasing the number of free charge carriers. This whole process is sped up due to the small thickness.

Ultrathin (less than 10 nm) WO\(_{3-x}\) nanoflakes were intercalated with H\(^+\) and tested as field-effect-transistor (FET) based devices.\[83\] Zhuiykov et al. reported that devices prepared this way reach charge-carrier mobility of 319 cm\(^2\)V\(^{-1}\)s\(^{-2}\), comparable to those of MoS\(_2\) and WS\(_2\), while for the nanoflakes before intercalation the mobility was 275 cm\(^2\)V\(^{-1}\)s\(^{-2}\). Both results are great improvements compared to the bulk WO\(_3\), that had the reported charge-carrier mobility of 12 cm\(^2\)V\(^{-1}\)s\(^{-2}\).\[84\] By changing the thickness of the material (from 50 nm to 2.5 nm), the bandgap was modulated from 2.60 to 2.40 eV. It is believed that the intercalated H\(^+\) ions interact with the corner-sharing oxygen atoms in the first monolayer, while the remaining ions get transferred deeper into the structure and repeat the same interaction. This fuels the formation of H\(_2\)O molecules that get released, leaving lone oxygen vacancies. The additional electron gets delocalized within the layers, giving rise to a mid-gap state. Furthermore, it was shown that H\(^+\) intercalation reduces the bandgap from 2.6 to 2.5 eV.

### 3.3 Photocatalysis and Photoelectrochemical (PEC) Water Splitting

Pristine WO\(_3\) does not have the photocatalytic activity high enough for practical use. Therefore, many approaches have been undertaken to improve the photocatalytic performance, with the most efficient ones being the introduction of the oxygen vacancies and/or using lower dimensional WO\(_{3-x}\).

The photocatalytic reduction of CO\(_2\) is an important route for its transformation to organic compounds as well as CO. Semiconductors have been used for photocatalysis with the absorption of a photon with the energy greater than its bandgap. This process induces an interband transition, where conduction band electrons and valence band holes are formed. The electrons and holes diffuse to the surface of the material, but only a fraction reaches it due to the recombination in addition, the free charge carriers that reach the surface may be trapped before the interfacial charge transfer. Lastly, the photogenerated electrons reduce the CO\(_2\) adsorbed on the catalyst surface into CO, HCOOH etc, while the holes oxidize H\(_2\)O to O\(_2\). One of the most important steps is the facilitation of the electron-hole separation, since the charge recombination happens on a much faster timescale (10\(^{-7}\) s) than the reaction process (10\(^{-3}\)–10\(^{-8}\) s).\[84\] Using the lower-dimensional WO\(_{3-x}\) can potentially improve the catalytic behaviour. Namely, in the case of bulk WO\(_3\), the photogenerated electrons in the conduction band have a lower, more positive, band-edge position.\[25\] Therefore, in bulk, this material cannot be used for the reduction of CO\(_2\) or H\(_2\)O. On the other hand, 5 nm thick WO\(_3\) nanosheets could catalyse the photoreduction of CO\(_2\) with H\(_2\)O into CH\(_4\). For such ultrathin material, the bandgap
increased from 2.63 eV to 2.79 eV, while the conduction band edge moved from 0.05 eV to −0.42 eV (versus normal hydrogen electrode, NHE), becoming more negative than the CO\textsubscript{2}/CH\textsubscript{4} redox potential at −0.24 eV.\textsuperscript{[25–26]} This demonstrates how a specific morphology can change the position of the conduction and/or the valence band, making the material a more suitable candidate for CO\textsubscript{2} reduction.

Liang \textit{et al.} studied 5 nm thick WO\textsubscript{3} sheets’ photocatalytic activity by degradation of methyl orange (MO) under simulated sunlight.\textsuperscript{[3]} They showed that the nanosheets have superior photocatalytic activity compared to nanoparticles or bulk material, due to their high specific surface area. Ultrathin (5 nm) WO\textsubscript{3–x} nanosheets with abundant surface oxygen vacancies were also tested as PEC devices, by degradation of MO under visible light.\textsuperscript{[14]} After 90 min of irradiation, 70% of the solution was degraded, making them good candidates for this type of catalysis.

WO\textsubscript{3–x} nanosheets with up to 300 nm lateral size and 15 nm thickness were tested as photocatalysts by using methylene blue (MB) and congo-red (CR) dyes under visible light irradiation.\textsuperscript{[61]} In 100 min, 99.5% of MB and 92% of CR was photodegraded by the nanosheets, a significant improvement compared with the nanorods (76% and 70%). The superior photocatalytic performance of the nanosheets is explained by the increase in the active surface, the smaller bandgap and oxygen deficiencies.

Both pristine WO\textsubscript{3} and 20–30 nm thick WO\textsubscript{3} nanosheets with oxygen vacancies were tested for their photocatalytic activity for the degradation of rhodamine B (RhB) under visible light irradiation.\textsuperscript{[47a]} While the pristine oxide decomposed only 9% of RhB after 320 min, WO\textsubscript{3} nanosheets with oxygen vacancies had increased photocatalytic efficiency of 77%. The latter sample had enhanced visible light absorption, and the plasmonic resonance with the peak at 800 nm. The oxygen vacancies act as electron donors and contribute to the enhanced donor density, increasing the charge transport and enhancing the photocatalytic activity.\textsuperscript{[47a]} Hydrothermally prepared WO\textsubscript{3} platelets with 50 nm thickness and up to 170 nm in lateral size were tested for the similar activity.\textsuperscript{[85]} It was shown that after 70 min of irradiation, the characteristic absorption peak of RhB almost disappeared, suggesting good photocatalytic activity.

Photoelectrochemical (PEC) water splitting is an increasingly popular technique for the efficient hydrogen generation. While the hydrogen is produced at the photocathode part of the PEC cell, photoanode material is responsible for the oxygen evolution reaction. Suitable photoanode candidates need to have appropriate band alignments (valence band more positive than water oxidation and conduction band more negative than hydrogen reduction) and to be absorbent in the visible light. WO\textsubscript{3} has a bandgap that can capture approximately 12% of the solar spectrum and absorb light up to 500 nm in the visible spectrum,\textsuperscript{[86]} while being chemically stable and environmentally friendly. In the case of the suboxides, the W\textsuperscript{5+} present in CS and PC structures as well as oxygen vacancy-induced electron traps can extend the photo-electron lifetimes, improving their performance as photocathodes for water splitting.\textsuperscript{[87]} As a result, the photogenerated holes in the valence band have more time to move to the electrode and participate in the reaction. The W\textsuperscript{5+} and oxygen vacancies are not just active centres which capture charges to block recombination, they may also reduce the activation energy. On the other hand, samples with high number of defects may have decreased crystallinity. This can result in an overall decrease of photocurrents due to increase in scattering effects. Since the hole diffusion length in WO\textsubscript{3} is 150 nm,\textsuperscript{[88]} if the thickness of the samples is of an approximately similar size, it can play a significant role in decreasing charge carrier recombination. If this is fulfilled, the photogenerated holes can reach the surface more easily and participate in water splitting before recombining.

The free-standing pore-rich sub-4 nm thick WO\textsubscript{3} nanosheets were obtained by using a chemical topology transformation strategy.\textsuperscript{[90]} It was demonstrated that they have more photogenerated holes, shorter migration path and stronger oxidation ability than thicker samples. The measured photocurrent density of this sample is 2.14 mA cm\textsuperscript{−2}.

Mohamed \textit{et al.} investigated both the stoichiometric and nonstoichiometric WO\textsubscript{3}, using an electrochemical method to study the nature of the defect states.\textsuperscript{[72]} Annealing the samples under different atmospheres resulted not only in different number, but in different nature of vacancies, making this a suitable approach to defect engineering. The highest photocurrent density was obtained on the nanoflakes annealed in air (1.3 mA cm\textsuperscript{−2}), with the optical band gap of 2.88 eV. It was demonstrated that the nonstoichiometric samples had higher photocurrents, indicating the presence of the shallow surface states, that feed the conduction band with electrons and form interband states. When the deep defect states become more dominant, they push the Fermi level away from the conduction band minimum, having damaging effect on the photocurrent. It can be concluded that the moderate concentration of oxygen vacancies results in appearance of W\textsuperscript{5+} shallow donor states that increase the photoactivity, while the deep trap W\textsuperscript{4+} states arise with the increase in oxygen vacancies, with the detrimental effect on photocurrent. This subtle interplay explains the contradictory results for the same material prepared under different conditions.

Soltani \textit{et al.} designed 50 nm thick highly porous WO\textsubscript{3–x} nanoplates with dual oxygen and tungsten vacancies for PEC water splitting.\textsuperscript{[87]} The number of oxygen vacancies and the film design were optimised to provide a large surface area for efficient charge collecting, which led to a photocurrent density of 4.12 mA cm\textsuperscript{−2} at 1.6 V vs Ag/AgCl. The stability time was reported as 1 h.

4. Summary and Outlook

In this review, an overview of the recent progress in the preparation of quasi-two-dimensional tungsten (sub)oxides was discussed. In recent years, a wide range of techniques...
were developed to synthesize such materials. To a certain degree, the crystal phase, morphology and stoichiometry can be controlled but there is still room for improvement. For example, as discussed above, different facets have unique physical and chemical properties, which can be exploited in a wide range of chemical reactions and sensing devices. As of now, only a few 2D-WO$_3$ nanomaterials were synthesized with the certain facets exposed intentionally. Although the majority of the tungsten oxide nanomaterials appears in one form of the WO$_3$ crystal structure, substoichiometric tungsten oxides (WO$_{3-x}$) show a great variety of structures. Furthermore, they hold great promise due to their W$^{3+}$ states that act as electron donors. By varying the stoichiometry of WO$_{3-x}$ or the number of oxygen vacancies on the surface of tungsten (sub)oxides, their electrical and optical properties can be tuned for specific devices and chemical reactions.

It has to be pointed out that in the majority of publications, the material’s reported stoichiometry was determined exclusively from XRD measurements, which is not a suitable method as the differences between the WO$_3$ phases are too small to be unambiguously detected. Furthermore, it should be emphasized that the WO$_{3-x}$ materials containing CS and PC structures should not be interchanged with materials with surface oxygen vacancies. Although individual oxygen vacancies can be produced, in order to minimize the surface energy, surface oxygen vacancies. Although individual oxygen vacancies can be produced, in order to minimize the surface energy, PC structures are formed while single CS planes appear when the material is further reduced. It would be beneficial if the reports on tungsten suboxide materials contained a thorough examination with HR TEM and electron diffraction techniques in order to determine the true nature and structure of oxygen vacancies. Only when this is achieved, further spectroscopic methods, such as Raman spectroscopy and optical measurements, can be utilized properly.

When it comes to potential applications, three of the most important factors that are responsible for the performance are the sample thickness, stoichiometry, and the oxygen vacancies. While the nanostructured suboxides in the shape of nanorods, nanowires and various other types of nanoparticles have been under numerous application-based studies, the similar research for their 2D counterparts is still in its infancy. For example, their charge-carrier densities are comparable to those of transition metal dichalcogenides, but the amount of reports of FETs based on these suboxides has been incomparably small. The control of the thickness, stoichiometry, and the introduction of the oxygen vacancies can be used as general strategies for increasing the electrical conductivity and photocatalytic activity. One of the major challenges could be the quantification and the effect on the crystal structure of the oxygen vacancies, and the deep understanding of their effect on optical and electronic properties, and the resulting performance in various applications.

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REVIEW

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Recent Progress in the Synthesis and Potential Applications of Two-Dimensional Tungsten (Sub)oxides