2D Tungsten Chalcogenides: Synthesis, Properties and Applications

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Layered transition metal chalcogenides possess properties that not only open up broad fundamental scientific enquiries but also indicate that a myriad of applications can be developed by using these materials. This is also true for tungsten-based chalcogenides which can provide an assortment of structural forms with different electronic flairs as well as chemical activity. Such emergence of tungsten based chalcogenides as advanced forms of materials lead several investigators to believe that a tremendous opportunity lies in understanding their fundamental properties, and by utilizing that knowledge the authors may create function specific materials through structural tailoring, defect engineering, chemical modifications as well as by combining them with other layered materials with complementary functionalities. Indeed several current scientific endeavors have indicated that an incredible potential for developing these materials for future applications development in key technology sectors such as energy, electronics, sensors, and catalysis are perhaps viable. This review article is an attempt to capture this essence by providing a summary of key scientific investigations related to various aspects of synthesis, characterization, modifications, and high value applications. Finally, some open questions and a discussion on imminent research needs and directions in developing tungsten based chalcogenide materials for future applications are presented.

1. Introduction

In recent years, 2D nanostructures, such as graphene and hexagonal boron nitride, and lately, thin sheets of transition metal dichalcogenides (TMDCs) have gained emerging attention fueled by their excellent properties and potential use in future electrical devices, optoelectronics and associated technologies. Their fascinating properties are the result of the layered structure held together by weak van der Waals forces similarly to graphene, however, in TMDCs one layer is much more complex; consisting of a hexagonal plane of transition metals (typically metals of group IV–VII) sandwiched between two planes of chalcogens (S, Se, and Te) by strong covalent bonds (Figure 1). In 2004, the pioneering isolation of graphene sheets[1] gave a tremendous boost to the scientific community scrutinizing similar layered materials which can be separated relatively easily to single-layers or so-called monolayers. Based on their unique electronic transport properties and advantageous band structure these materials are suggested to have a great number of applications in transistors,[2–4] solar cells,[5–7] optoelectronic devices,[8,9] catalysts,[10] and sensors.[11] As might be anticipated their properties at atomic scale, greatly differ from their bulk counterpart. Recently, monolayers of MoS2 and WS2 have been found to exhibit direct semiconducting band gap in the visible spectrum rather than an indirect one that is well-known for their bulk phase.[12] In addition to material thickness, the band gap can be further fine-tuned, implying also beneficial changes in material properties, by doping TMDCs with different chalcogen atoms. As an example, when the thickness of MoS2 is reduced from bulk to monolayer a significant increase in the band gap can be observed, from $\approx$1.2 to $\approx$1.8 eV,[12] accompanied with an indirect-to-direct transition, and as expected, single layers also exhibit...
enhanced photoluminescence behavior. Their electrical properties also vary from insulating (HfS₂) to metallic behavior (NbS₂ and VSe₂) depending on the crystal structure and the number of transition metal d-electrons. Although, in the TMDCs family, molybdenum disulfide has been subjected to the most intensive research, recently, it has been demonstrated that, akin to MoS₂, the electronic structure of WS₂, WSe₂, and MoSe₂[13,14] and thus their electrical transport, optical and optoelectronic properties are strongly influenced by the number of layers,[15] microstructure, routes of synthesis and electrical contacts among many others (Table S1, Supporting Information).

Accordingly, in this review, we summarize the contemporary literature of tungsten dichalcogenides with the aim of unleashing their complex structure dependent properties, and highlighting the implications of those for practical applications in nano and optoelectronics, (electro)catalysis, and chemical sensors.

2. Structure and General Characterization

Typically, the unit cell structure of TMDCs is either trigonal prismatic (hexagonal), 2H or D₃h, or distorted hexagonal also known as octahedral structure (1T or D₃d). The 2H unit cell is extended over two chalcogen-metal-chalcogen layers, whereas in 1T there is only one layer in a unit cell.[16] Which of these two lattice structures is more stable depends on the constituent metal and chalcogen atoms. In general, one can say that TMDCs formed of group IV metals are nonmagnetic semiconductors that are only stable in trigonal structures.[17] Albeit, the reversible transition to octahedral unit cell structure is possible, through chemical modification (for example exfoliation),[18,19] it can distort the lattice structure. The significance of the unit cell structure is clearly demonstrated by the semiconducting nature of 2H-MoS₂ compared to the metallic one of 1T-MoS₂,[20] consequently the unit cell structure affects the attributes of these materials largely. Although the research field related to TMDCs is extremely broad; including a large number of different combinations of metals and chalcogens, taking shape in interesting morphologies varying from 3D to 1D (nanotubes, nanobelts, nanowires, nanoparticles etc.); yet in this review, we are concentrating only on 2D sheets and flakes of tungsten dichalcogenides (WS₂, WSe₂, and WTe₂). Till today, layered tungsten dichalcogenides (WX₂) have not been studied to such an extent as 2D molybdenum dichalcogenides mainly due to their higher melting point and therefore more difficult sublimation of WO₃ (and W) compared to MoO₃ (and Mo), most commonly used reactants for tungsten and molybdenum dichalcogenide synthesis.[21]

As the layer thickness of TMDC is reduced, the reflection (002) cease to appear on the XRD pattern, making this technique a convenient tool in verifying the formation of few-layered flakes, though differences between mono-, bi-, and few-layered TMDCs cannot be achieved.[22] Contrary, high resolution scanning transmission microscopy is a quite practical tool to resolve the details of both micro and structure. It is possible even to identify and distinguish 2H and 1T phases.[19]

In general, Raman spectroscopy is known to be one of the most useful methods analyzing low-dimensional structures and identifying the number of layers in TMDCs.[23] In a typical spectrum, two characteristic peaks can be identified: i) A₁g caused

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by the chalcogen atoms moving of the plane in opposite directions while metal atoms, situated between them, stay stationary, and ii) $E_{2g}^1$ attributed to the metal and chalcogen atoms moving in-plane, in opposite directions. If the TMDC comprises of several layers, shift in both peaks occurs ($E_{2g}^1$ mode undergoes a redshift, whereas the $A_{1g}$ mode shows blue shift) since the extra layers stiffen the out-of-plane movement and help in relaxing the in-plane movement. It has to be noted, that in some reports on WS$_2$ and WSe$_2$ only the $A_{1g}$ mode was found to be thickness dependent while the position of the $E_{2g}^1$ mode was stated stationary. Similarly, orthorhombic WTe$_2$ is an exception; when its thickness is reduced, beside the in-plane $A_{1g}$ mode, a shift for all other vibrational modes is observed. Furthermore, the lack of some Raman peaks, identified in the case of the bulk phase, provide a reliable method to distinguish mono- and bilayer WTe$_2$ (Figure 2). Differences in Raman spectra are understandable since the vibration modes are completely different for 1H and 1T structures. Further influential factors on the appearance of Raman spectra can be caused by temperature, carrier concentration and strain in the lattice.

Room temperature photoluminescence spectroscopy (PL) is not sensitive enough to determine the quality of monolayer crystals, and therefore low temperature PL is required in order to reveal PL behavior of such materials. A typical PL spectrum of WSe$_2$ monolayer shows three distinguished features: i) a high energy peak ($X^0$) at 708 nm caused by excitation emission, ii) a high energy peak ($X^*$) at 722 nm corresponding to charge excitation emission, and finally iii) a broad emission peak caused by the emission of impurity/defect-trapped excitons.

Photoluminescence measurements show that similar to MoS$_2$ both WS$_2$ and WSe$_2$ exhibit a transition from indirect to direct band-gap as the thickness of the materials is decreased.
from multilayers to monolayers. The PL intensity is decreasing ≈3 orders of magnitude with the number of layers from 1L to bulk (Figure 3a,d). Apart from the peak of indirect transition (I), two other peaks appear in the spectra at higher energies: one is due to a direct transition (A) and another caused by hot PL (B) (Figure 3b,e). The broadening of these latter peaks suggests an excitonic origin similar to that in MoS2. Furthermore, the nearly constant energy difference of ≈400 meV between A and B (Figure 3c,f) suggests limited interlayer hopping in both WS2 and WSe2 ultrathin thin films. Ab initio calculations indicate that such thickness independent splitting is due to the giant spin-valley coupling which indeed suppresses interlayer hopping at the K points of valence band edge.[27]

3. Synthesis of Tungsten Dichalcogenides

In theory, the crystal structure of TMDS enables relatively easy isolation of thin layers since the chalcogenide-metal-chalcogenide layers are attached by weak van der Waals force. Yet, experimental preparation of single layer films has been hindered by the inherent inclination of these materials to form multilayers or nanotubes. Initially, mechanical and chemical exfoliation,[15,34,35] with very low yield, were applied to separate monolayers from the bulk material while in the last few years, the most attention has been devoted to a novel method, namely to thermal-sulfurization of thin layer of corresponding metal oxides.[8,36,37] One of the major problems associated with the preparation of monolayers of TMDCs, is the difficulty in achieving industrial quality monolayers required for large scale production of TMDCs based electrical applications.

In order to exploit the beneficial properties of 2D tungsten dichalcogenides, its layers have to be separated from each other. Unfortunately, the production of large quantities of uniform mono-, bi-, or few-layered materials can be challenging and costly. Currently available large variety of different approaches can be divided into two major categories: top-down exfoliation of layers from bulk material, and bottom-up synthesis of layers from reactants. To fully exploit the unique properties of these materials for future applications, such procedures are required to have control over the crystal size, quality, and thickness. It is generally agreed that the material quality specifications highly depend on the particular application, while some require large quantities others need appropriate well-defined shaped monolayers, and as such the selection of the most suitable approach can be extremely challenging. Nevertheless, in this section we will make an attempt to provide a comprehensive review on the various synthesis methods of 2D tungsten dicalkogenides (Figure 4).

3.1. Top-Down Methods

Micromechanical cleavage became known instantly by the scientific community, when the first graphene flake was exfoliated.
by Scotch tape from the surface of highly ordered pyrolytic graphite (HOPG).\cite{1} It is not surprising that such a simple method was adapted for the cleavage of thin flakes of other weakly bonded layered materials, as well as for tungsten chalcogenides (WS$_2$,\cite{29} WSe$_2$,\cite{39} WTe$_2$\cite{40}). Although such procedure can provide high quality, thin layers of crystals, it suffers from a great number of drawbacks as it is time-consuming, can produce only low quantity, and has poor reproducibility.

In order to produce large amount of TMDCs nanosheets liquid phase exfoliation assisted by sonication has proven to be a promising method. Throughout this treatment, van der Waals forces keeping together the layers in the bulk, are weakened by chemicals such as solvents like n-methyl-2-pyrroldione (NMP),\cite{35,41} n-cyclohexyl-2-pyrrolidone (CHP),\cite{42} sodium naphthalenide (NAPH), \cite{43} sodium cholate, \cite{44} (Figure 5) or water mixtures.\cite{45} Intercalation of ions,\cite{41} such as lithium,\cite{23} expanding the layer distance and thereby creating strain in the lattice, is commonly applied as well (Figure 6). Albeit dispersing bulk WSe$_2$ and WS$_2$ in NMP has shown to produce few layered flakes,\cite{35,41} from monolayer to tens of layers, yet as the formed nanosheets are often heterogeneous in quality it limits their use in most of the applications. Ion intercalation applying

**Figure 4.** Strategies for the formation of monolayers of transition metal dichalcogenides including top-down chemical/mechanical exfoliation as well as bottom-up chemical vapor deposition, powder vaporization, metal transformation, chemical vapor transport, pulsed laser, deposition, molecular beam epitaxy, spray pyrolysis, and electrochemical synthesis. Reproduced with permission.\cite{38} Copyright 2015, Annual Reviews.

**Figure 5.** a) Dispersions of WS$_2$, MoSe$_2$, NbSe$_2$, TaSe$_2$, and h-BN stabilized in aqueous sodium cholate and b) their optical absorbance. c) Thin films of tangled networks of filtered nanoflakes of the corresponding materials. d–i) Transmission electron micrographs of the single-layer flakes. Reproduced with permission.\cite{46} Copyright 2011, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
lithium cations is typically done using expensive n-butyllithium as an intercalation agent.\textsuperscript{[23,41]} Once lithium ions have intercalated between the layers, the material is washed with water which on the one hand will remove the excess n-butyllithium (BuLi), on the other hand it will also react with the intercalated lithium resulting in lithium hydroxide and hydrogen gas, eventually pushing the layers apart. Lithium intercalation as such has been shown to be effective to produce mono- and bilayered WS\textsubscript{2} flakes,\textsuperscript{[53]} nevertheless the same method applied to WSe\textsubscript{2} eventuated flakes with thickness of several micrometers.\textsuperscript{[44]} Limitation of this approach lies in its long reaction times and elevated reaction temperatures.\textsuperscript{[43]}

Electrochemical lithiation has been found as an efficient route to produce large quantities of single-layer WS\textsubscript{2} nanosheets.\textsuperscript{[46]} The bulk layered material was used as the cathode, whereas lithium foil served as the anode, providing intercalating lithium ions and LiPF\textsubscript{6} was applied as the electrolyte. As soon as current was conducted between the electrodes the lithiation process started, after which the material was washed and exfoliated. While traditional lithium intercalation process takes several days to have fully intercalated the above described electrochemical process can be accomplished in a few hours. Possibility of its facile scale-up, by increasing the size of the electrodes, can be attributed as a further advantage of this synthesis procedure. Even though lithium intercalation is considered as an efficient way to produce high amounts of well-controlled nanosheets, the flammable nature and expensive price of lithium, urge the scientific community to find a replacement for this approach.

Although exfoliation is a conventional method to produce large quantities of nanosheets, yet structural phase transformations from 2H to 1H during intercalation process can make the process unreliable. The nature of intercalation agent has significant impact on the degree of exfoliation as well as on the phase transition of the material.\textsuperscript{[54]} For instance, exfoliation of WS\textsubscript{2} in BuLi the concentration of IT-WS\textsubscript{2} is \(\approx 10\) at.\% of, whereas in NAPH it is significantly higher \(\approx 37\) at.\%. Interestingly, the NAPH exfoliated WS\textsubscript{2} showed room temperature ferromagnetism, which was not detected for BuLi exfoliated samples or for the bulk material.

Other uncommon chemicals to exfoliate bulk WS\textsubscript{2} include supercritical CO\textsubscript{2},\textsuperscript{[45]} but also concentrated chlorosulfonic acid\textsuperscript{[48]} has been suggested to produce few-layered nanosheets. This latter can provide stable and highly concentrated dispersions compared to those in NaDBS, propanol or sulfuric acid, however its major disadvantage is the protonation of the nanosheet surface.

### 3.2. Bottom-Up Synthesis

Other useful routes producing 2D tungsten dichalcogenides are such "bottom-up" methods as chemical vapor deposition (CVD), powder vaporization, metal transformation and chemical vapor transport. These techniques apply high temperatures to facilitate the decomposition of precursors, diffusion and reaction of the participating atoms, and formation of crystalline products. The differences among these methods are only the way of delivery of the precursors.

In CVD, both metal and chalcogen precursors are vapors, which react in the gas phase and deposit on a substrate to form the crystalline product.\textsuperscript{[21,49,50]} Notable examples of substrates include SiO\textsubscript{2},\textsuperscript{[28]} Si\textsubscript{3}N\textsubscript{4},\textsuperscript{[51]} sapphire, quartz, and graphene\textsuperscript{[16,37,50]} offering a good selection of surfaces suitable for any particular application. In powder vaporization, oxides of the metals are vaporized and reacted with the chalcogens (either vapors or precursors), which then deposit and grow crystals on supports. In the case of metal transformation, solid metals are first deposited on the substrate, and then exposed to vapors of chalcogens at temperatures typically above 600 °C. Another approach is an application of solid chalcogen film over the metal for solid-solid reactions at high temperatures.

The presence of different molecules seems to play an important role as promoting agents during the formation of 2D tungsten dichalcogenides, although the exact mechanisms remain elusive in many cases. In order to grow highly crystalline monolayers of WSe\textsubscript{2} by selenization of WO\textsubscript{3}, hydrogen gas has shown to have a crucial role as an activating agent.\textsuperscript{[55]} Crystal growth starts by the reduction of WO\textsubscript{3} to volatile WO\textsubscript{2}, which reacts with vaporized Se followed by the formation of WSe\textsubscript{2} layers. Similarly, in the case of WS\textsubscript{2} the reaction, a small amount of H\textsubscript{2} has shown to influence the shape of the growing crystals, making those more symmetric by affecting the growth process.\textsuperscript{[55]} Not only H\textsubscript{2} but also additional sulfur has been shown to promote the formation of mono- and few-layered WSe\textsubscript{2} flakes during the CVD synthesis.\textsuperscript{[54]} As evidenced by some research groups CVD process based on organic tungsten and selenium precursors result in thick
tungsten dichalcogenide films. There are only a few reports of large-area mono- or few-layers of WSe₂ using metal-organic compounds as precursors. In the course of the growth process, pure H₂ as a carrier gas is favored in order to prevent the formation of carbon impurities originating from organometallic compounds. However, it is worth noting here that Kang et al. recently managed to grow 4-inch WS₂ monolayer films on Si wafer in diluted H₂ gas. The key strategy for this procedure was to carefully monitor the concentrations of each chemical throughout the synthesis by regulating the partial pressures.

Another useful route to the large area, triangle crystals WSe₂ growth is the physical vapor deposition (PVD), for which case bulk WSe₂, instead of some precursor, is used as a raw material to synthesize WSe₂ monolayers on a substrate. The growth mechanism shares some similarities with that of the chemical vapor deposition and transport processes, hence the shape of the crystals can be controlled by altering the carrier gas mixture or precursor ratios. As it might be anticipated, parameters, such as flow rate, temperature, pressure and time, moreover the nature of the substrate all has their influences on the quality of the resulting product.

Ultra-narrow WS₂ nanoribbons with layer thickness of one to few was reported by Wang et al. exploiting narrow carbon nanotubes (CNTs) as a growth template. To begin with CNTs are opened, followed by the introduction of organometallic tungsten precursor in H₂S/H₂ atmosphere at high temperature (800 °C). The layer thickness of nanoribbons is determined by the inner diameter of the CNT used as a template, accordingly monolayered WS₂ nanoribbons are synthesized in single-walled carbon nanotubes (SWCNTs) while bilayered ones are formed in double-walled carbon nanotubes (DWCNTs) having larger inner diameter than the SWCNTs. The length of nanoribbons varied between tens to hundreds of nanometers, whereas the maximum width was found to be around 3 nm. Both armchair and zigzag forms of nanoribbons were detected, latter one being the more stable.

In all above described examples, the growth direction of the crystal layers has been horizontal, parallel to growth substrate. Vertical growth of TMDCs can be achieved by the modification of the metal seed layer thickness on the substrate, since substrates with low nucleation density favor the formation of vertical growth over horizontal.

Although there are several other methods to prepare tungsten dichalcogenide nanostructures such as microwave assisted wet chemical approaches, sonochemical and hydrothermal synthesis, the products gained through these methods are not 2D materials but nanowires, nanorods, nanoparticles, or layered flower-like structures. Up to now, there are only a couple of reports describing wet chemical synthesized 2D tungsten dichalcogenides. A simple way of producing WS₂ nanosheets was shown by applying WCl₆ and thioacetamide as precursors in a hydrothermal process (265 °C for 24 h). The as formed few-layered nanosheets had a typical thickness of 1–3 nm and a lateral length of 0.5–1 μm. Another simple, yet unique wet chemical approach was proven to produce either metallic 1T-WS₂ or semiconducting 2H-WS₂ monolayers, depending on the synthesis conditions. The precursor solution includes WCl₄, oleyamine, and oleic acid, in which carbon disulfide (CS₂) serving as a sulfide source and reducing agent is added at 320 °C. At the initial phase of the reaction dithiocarbamate forms, and after thermal decomposition WS₂ forms. Depending on the reactivity of tungsten precursor, controlled by the coordination ligand, the 1T-WS₂/2H-WS₂ ratio of the product can be adjusted.

### 4. Properties

Replacing sulfur with larger atomic size elements of the oxygen group (i.e., Se and Te), the metal-chalcogen bond length as well as the in-sheet lattice constant increase while at the same time, the band gap decreases in the same order (Tables 1 and 2). In the family of WX₂, preparation of

| Mₓ₂ | Band gap monolayer (eV) | VBM/CBM (eV) | Fermi level (eV) | Electron affinity (eV) | Work function (eV) |
|-----|------------------------|--------------|-----------------|-----------------------|-------------------|
| WS₂ | n-type, semiconductive | 2.1 eV[90] (1.3 eV) | -5.50/-3.96 | -4.75 | 3.9[72] |
| WSe₂ | p-type[8], n-type; ambipolar[8] semiconductive | 1.6-1.7 eV[10] (0.9-1.2 eV) | -4.87/-3.54 | -4.25 | 3.5[72,73] |
| WTe₂ | semimetallic, diamagnetic metallic | 0.7 eV–0.9 (Td 0.21 eV; 2H 0.7 eV)[46] | 2H -4.44/-3.69 | 2H -4.0 | 3.65[74] |
|       |                        |              |                 |                       | 4.06 Td –4.39; 2H -4.45[74] |

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tungsten sulfides is known to be easier than that of other tungsten chalcogenides, simply due to the fact that sulfide precursors are more reactive than selenides or tellurides. Furthermore, the increasing stability of the tungsten dichalcogenide sheets in order \( \text{WTe}_2 < \text{WSe}_2 < \text{WS}_2 \) also explains the facile synthesis of tungsten sulfide sheets.[70] The thickness of TMDC monolayer typically falls into the 0.6–0.7 nm range, whereas their lateral dimension greatly depends on the applied synthetic procedure.

### 4.1. Tungsten Disulfide and Tungsten Diselenide

Regarding the band gap of \( \text{WS}_2 \) and \( \text{WSe}_2 \), similarly to \( \text{MoS}_2 \) monolayers, indirect to direct transition is observed, when the layer thickness is reduced to monolayers. Accordingly, single-layers of the aforementioned materials are more efficient phonon absorbers and emitters than their bulk counterparts.

| MX_2       | a [Å]     | M–X [Å]   | h (Å) | Crystal system | Space group |
|------------|-----------|-----------|-------|----------------|-------------|
| WS\(_2\)   | 3.16–3.19 | 2.39–2.42 | 6.08–6.18 | Hexagonal       | P6\(_3/mmc\) |
| WSe\(_2\)  | 3.29–3.32 | 2.51–2.55 | 6.41   | Hexagonal       | P6\(_3/mmc\) |
| WTe\(_2\)  | 3.47–3.56 | 2.70–2.74 | 6.94–7.03 | Hexagonal       | orthorhombic |

The band structures as the function of different layer thickness (Figure 8) clearly reveals that only monolayers own a direct band gap, whereas in double and higher numbers of layers it turns into indirect. To be more exact, the valence band maximum (VBM) and the conduction band minimum (CBM) of the bulk phase are located at the \( \Gamma \)-point and between the \( \Gamma \)- and the \( K \)-points, respectively; on the contrary, both VBM and CBM of single layer shift to the \( K \)-point therefore the \( k \)-vectors become the same.

The transport properties of \( \text{WSe}_2 \) are strongly influenced by the type of the contact metal and by the preparation method. For example, mechanically exfoliated \( \text{WSe}_2 \) monolayers were found to be n-type,[84] whereas CVD grown \( \text{WSe}_2 \) monolayers, contacted using palladium shown p-type behavior whereas with gold or titanium contacts the behavior was found to be ambipolar.[21] Back gated FETs were prepared using the 2D \( \text{WSe}_2 \) flakes directly grown on Si/SiO\(_2\) substrates. Various contact materials were tested, deposited using e-beam lithography including Pd/Ti (50 nm/0.5 or 1 nm), Au/Ti (50 nm/0.5 or 1 nm), and Ti/Au (5 nm/50 nm).[21] Looking forward we note that the ability to manipulate the properties of such 2D materials by simply altering the material contacts carries large potential for forthcoming electronic and optoelectronic devices.

As for \( \text{WS}_2 \), both n and p-type semiconducting behaviors were reported. The crystal seems to be highly sensitive to the surroundings and impurities. Slight doping of reactive sputter deposition grown \( \text{WS}_2 \) mono and few-layered crystals with N atoms results in a switch from n to p-type behavior[85]

![Figure 8](image-url)
Heterostructures of WS$_2$ nanowires and nanoflakes obtained by the sulfurization of WO$_3$ nanowires showed p-type properties.\cite{86–88} In addition, doping WS$_2$ lattice with Ta atoms changes the electrical properties of the material from semiconducting to metallic.\cite{70}

Room temperature ferromagnetic behavior of WS$_2$ monolayers was detected for both NAPH\cite{43} and DMF\cite{89} exfoliated samples. Interestingly, few-layered WS$_2$ and WSe$_2$ were found to have some ferromagnetism when exfoliated in DMF.\cite{90} This peculiar magnetism on the one hand was speculated to be caused by the phase transition from 2H-WS$_2$ to 1T-WS$_2$, on the other hand exfoliation resultant high amount of nanosheet edges and high degree of disorder were also named as inflicting parameters.\cite{91–93} Although the reported ferromagnetic values are relatively low ($\approx 10^{-3}$ emu g$^{-1}$), nevertheless such phenomenon was detected neither for bulk nor for WS$_2$ exfoliated in other solvents.

4.2. Tungsten Ditelluride

Tungsten ditelluride differ greatly from other tungsten dichalcogenides since it has the lowest energy when crystallized in distorted 1T lattice structure shown in Figure 9 (also known as Td), having $\approx 0.075$ eV lower energy per unit than that of 2H-WTe$_2$.\cite{77} Compared to other TMDCs both bulk and monolayer form of Td-WTe$_2$ have similar semimetallic band structures, caused by small electron and hole pockets along the $\Gamma$–X direction.\cite{94} Theoretical studies of Augustin et al.\cite{95} and Ghosh et al.\cite{96} have demonstrated that Td-WTe$_2$ has both semimetallic and metallic nature. The first one is due to the partial overlapping of Te 5p and W 5d bands, whereas the latter is attributed to the classical metallic bands. Electrical properties of WTe$_2$ nanoribbons, when assumed to have hexagonal structure, depends on the arrangement of atoms in the lattice. Similarly to WS$_2$ nanoribbons,\cite{59} zigzag structure WTe$_2$ nanoribbon exhibits metallic behavior while atoms forming armchair structure will result in a semiconducting\cite{96} material.

The low density of states at Fermi level (Figures 9 and 10) is responsible for the surprisingly low conductivity of 2D WTe$_2$ structures, however, high pressure synthesis process, can eventuate low temperature superconductive behavior.\cite{97,98} The large magnetoresistance of single crystal WTe$_2$ can be reduced at the expense of greater pressure.\cite{97} Moreover, further increasing the pressure a critical value is reached at 10.5 GPa, where magnetoresistance will be turned off completely, generating

![Figure 9. a) Trigonal prismatic coordinated 2H-WTe$_2$ structure and b) octahedrally coordinated Td-WTe$_2$ structure. The electronic band structures of c) WTe$_2$ in the 2H structure has an indirect 0.70 eV bandgap, whereas in the d) Td structure has a 0.21 eV band overlap in $\Gamma$–X and the corresponding density of states e) reaches a minimum, but not zero at the Fermi level. Reproduced with permission.\cite{40} Copyright 2015, Springer Nature.](image-url)
a superconductive material. In situ Hall coefficient measurements revealed that with increasing pressure, while no phase transitions were observed, the number of hole carriers decreased at the same time the number of electron carriers increased. WTe$_2$ follows a dome-shaped superconductivity phase, emerging at 2.5 GPa.\footnote{98} Further elevating the pressure, the maximum critical temperature ($T_c$) of 7 K is attained at around 17 GPa, after which, monotonous decline of the $T_c$ is observed with the escalating pressure.

The extraordinary transport properties of WTe$_2$ manifested at low temperature can be accounted for the approximately similar size of electron and hole pockets at the Fermi level and the resultant perfect balance of electron and hole populations. Accordingly, the extremely large quadratic magnetoresistance reported for single crystals of WTe$_2$, showing no signs of saturation up to 60 T, is caused by the temperature dependent charge compensation of the transport.\footnote{94,100,101} Obviously such unique magnetoresistance could open up new opportunities in spintronic, and in low-temperature magnetic-field sensing applications as well.

### 4.3. Modification of Properties

Introduction of mechanical strain to the lattice can significantly change the electronic band structure and thus materials properties. Application of even small (1–2\%) compressive strain to the lattice of WX$_2$ monolayers can significantly change the band structure.\footnote{102} Ab initio calculations revealed that tungsten chalcogenides behave in a similar fashion as their molybdenum based counterparts (Figure 11).\footnote{78} Both tensile and shear strains induce a reduced band gap, and upon homogeneous biaxial tensile strain of \approx 10\% a semiconductor-to-metal transition occurs.

It is worth pointing out, that the electrical, mechanical (Poisson’s ratio, in-plane stiffness) and optical properties of monolayer WTe$_2$ (distorted T-phase) are anisotropic.\footnote{77} Introduction of small parallel strain (1\%) WTe$_2$ changes the semimetallic properties to semiconducting, whereas the perpendicular strain has no influence on the properties. Also, the imaginary part of the dielectric function shows different behavior depending on the direction of strain. Promising applications in the field of mechanical sensors\footnote{96} is foreseen for WTe$_2$ nanoribbon owing to its unique ability to change its band gap when defects, wrap, twist or ripple is introduced.

#### 5. Applications

##### 5.1. Field-Effect Transistors

Transistors are among the most important applications of semiconductors. Thus, their high structural stability, dangling bond free surface and high carrier mobility make semiconducting TMDCs promising candidates in such devices. Furthermore, their mechanical flexibility and reasonably good optical transparency are additional advantages raised great interest in the...
One excellent example is a 2D flexible and transparent thin film transistor (TFT) applying graphene metal electrodes, h-BN (hexagonal boron nitride) gate dielectric and bilayer WSe$_2$ as a semiconducting channel. The mobility values reported for the WSe$_2$ based device were $\approx 100$ times better than those of typical amorphous silicon based TFTs, and at the same time its $I_{ON}/I_{OFF}$ ratio was $10^7$. The device was stable under a broad temperature range and more than 88% transparent over the visible spectrum. All these results made it very clear that these materials may revolutionize micro and nanoelectronics and necessitate further efforts to the scrutiny of WS$_2$ and WSe$_2$.

Suitability of WS$_2$ monolayer for a field-effect transistor (FET) application, grown straight onto SiO$_2$ substrate, was studied by Kang et al., and although the synthesis parameters of the material was not fully optimized, the n-type FET showed relatively high field-effect mobility ($18 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), $I_{ON}/I_{OFF}$ current ratio ($10^9$) and also current saturation. Similar $I_{ON}/I_{OFF}$ ratios were reported for WS$_2$-FETs by another group, moreover in this case even higher field-effect mobility values were achieved: $50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature; $140 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $300 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at $-205 \text{ °C}$ for monolayer and bilayer devices, respectively. The dielectric environment of WS$_2$ flakes affects the field-effect mobility as demonstrated by Withers et al., comparing devices having SiO$_2$ and BN/SiO$_2$ gate dielectrics. The mobility and $I_{ON}/I_{OFF}$ ratio of monolayer WS$_2$ FETs can be further improved by sandwiching the WS$_2$ monolayer between h-BN layers. Thereby, mobility values as high as $214 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (at room temperature, with an $I_{ON}/I_{OFF}$ ratio of $10^7$) and $486 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (at $-268 \text{ °C}$) could be achieved. The h-BN layers not only provided an ideal substrate for the WS$_2$ monolayer but also served as protection from doping by air and other impurities. Similarly, in the case of n-type monolayer WSe$_2$ FET with Ag contacts, an extra layer of Al$_2$O$_3$ deposited on the channel area showed superior behavior ($I_{ON}$ of $205 \mu\text{A \mu m}^{-1}$ and mobility of $202 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) compared to a device without Al$_2$O$_3$ ($I_{ON}$ of $110 \mu\text{A \mu m}^{-1}$ and mobility of $48 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Here, the additional Al$_2$O$_3$ provided high-$\kappa$ dielectric environment and suppressed Coulomb scattering. Although one of the highest values, $I_{ON}$ of $210 \mu\text{A \mu m}^{-1}$ and mobility of $142 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, were reported of WSe$_2$-FET with In contacts and Al$_2$O$_3$ gate dielectric yet applying indium has its downsides such as poor adhesion and also low melting point (<160 °C), which makes it a quite unpractical contact material.

WS$_2$ monolayers enable the construction of both n- and p-type FETs; and consequently, inverter structures. In addition, the better resistance of selenides to oxidation in reference to their sulfide counterparts, make these even more attractive for practical applications. Consequently the above mentioned qualities contributed significantly to the extensive scientific interest toward WSe$_2$ as a channel material.
compared to other candidates of the tungsten dichalcogenide family. Yet, WSe2 based electrical devices suffer from typical challenges, such as the high Schottky barrier formed between WSe2 and contact metal, that so far hindered its evolution and implementation into commercial products. To overcome this obstacle, two main approaches are considered. On the one hand, contact metals with appropriate work function need to be chosen in preference to the type of the device. Accordingly, materials with high (low) work function in p-type (n-type) FETs are used to minimize the Schottky barrier. On the other hand, doping the contact region may be a further approach to reduce the barrier width.[84,114]

Efforts have been devoted to compare the temperature dependent field-effect mobility and hole Hall mobility of few layered (9–15 layers) WSe2-FET on p-doped Si.[115] The maximum field-effect mobility of ≈350 cm2 V−1 s−1 can be reached at room temperature while for Hall mobility for the maximum of 650 cm2 V−1 s−1 lower temperature is required as at room temperature the latter value drops significantly to ≈200 cm2 V−1 s−1.

The tunnel field-effect transistors (TFETs) are other promising candidates of future devices due to their small sub-threshold swing and low IOFF which both reduces power consumption. On a flexible and transparent substrate, TFET was built based on two graphene layers separated by WSe2 (acting as a barrier between the graphene contacts).[71] Interestingly, the highest ION/IOFF ratio (107) was measured, when the number of layers was four or five. According to the systematic calculations,[127] in which different n-type sources (Mo and W chalcogenides) were combined with p-type contacts (Ti, Zr, Hf, V, Nb, Ta chalcogenides), the best combination for vertical TFET was found to be W or Mo telluride and selenide combined with Zr or Hf selenide or sulfide. Simulation results suggest that WTe2 monolayer TFET might have better performance than TFETs based on other TMDCs.[117] Due to the smaller band gap and the effective mass of electrons and electron holes, the ION of the device is remarkably higher for WTe2 than that for WSe2 (127 μA μm−2 versus 4.6 μA μm−2). The performance can be further increased, reaching ION of 350 μA μm−2, by doping the WTe2 lattice; moreover, it should be pointed out that its unique combination of properties makes WTe2 potentially applicable in both homogenous and heterojunction n- and p-type TFET devices[118] with the highest ION performance.

The possibility of altering the n- or p-type behavior of WSe2-FET just by the selection of the contact material allows the realization of complementary inverters by the insertion of n-type and p-type FETs on the same WSe2 flake arranged in a double gated transistor geometry.[111,112] Typical contacts in p-type FETs are high work function metals such as Pt and Pd, in contrast, n-type construction can be enabled applying potassium doping the underlapped contact regions[83,111] (Figure 12) or using Ni instead.[110] Thus, a combination of the two on the same substrate provides the great opportunity as a platform for complementary metal-oxide-semiconductor (CMOS) devices and logic gates. As a result, typically dc voltage gain of WSe2 based inverters is ≈2[52,111] and value as high as ≈25 was reported for structures based on bilayer WSe2.[112] ION/IOFF ratios and mobilities over 102 and 200 cm2 V−1 s−1, respectively, were accomplished in a single n- and p-type FET device relying on h-BN passivated WSe2 channels and ionic liquid gated graphene contacts.[109] The work function of graphene was tuned by doping to minimize the height of the Schottky barrier at the graphene/semiconductor interface. Likewise, high carrier mobility as well as electron and hole mobility values of 90 and 7 cm2 V−1 s−1, respectively, were demonstrated when exploiting the benefits of ion gel, having high ionic concentration, applied as a gate in ambipolar WSe2 monolayer electric double-layer transistor.[52]

Optoelectronics devices able to generate, sense, control, or interact with light including solar cells, light-emitting diodes (LEDs) and photodetectors. Typically, materials having a direct band gap, large electron-hole pair binding energy and strong photoluminescence are promising candidates for such applications. In addition, a wide variety of transparent and flexible components are required for the realization of flexible and transparent optoelectronics, among them flexible, thin 2D TMDCs with typically direct and tunable bandgap are promising candidates. Photons having larger energy than the band gap can create either bound excitons or free carriers depending on their binding energy in the semiconductor, and therefore a direct band gap is demanded to achieve efficient absorption or emission of phonons. In contrast, for indirect bandgap, phonon absorption and emission process is less efficient owing to the required additional phonon participation to conserve the momentum. Since p-n junction is the functional element of many optoelectronic devices thus a considerable amount of efforts have been devoted to studying the interfacing behavior of WSe2 monolayer by electrostatic tuning.[120–123] Their abundance coupled with their direct bandgap in the visible range makes TMDCs an appealing light absorbing material for alternative thin film solar cells, including flexible ones suitable to cover buildings and curved surfaces. Further advantages of the WDCs family include photostability under excitation and environment-friendliness.[124,125] Although high energy conversion efficiency of WS2 solar cells were reported yet despite the technological advances it remains a great challenge to eliminate recombination centers at the surfaces perpendicular to the c-axis. For instance, a stable nanocomposite of 100 nm thick TiO2 layer sensitized using 5 nm thick WS2 was investigated as a potential absorber layer for electrochemical solar cells, however as the flow of the photocurrent is blocked at the direction perpendicular to the van der Waals surface of the WS2 layer, into the electrolyte, the device efficiency is significantly reduced. The efficiency of excitonic solar cell based on WDCs may vary depending on the composition of the applied materials; for, for example, MoS2/WS2 bilayer can attain power conversion efficiencies of 0.4–1.5%[124] while this value for MoS2/WSe2 was showed to be as low as 0.2%.[127] Similarly, the power conversion efficiency of 0.5% was achieved of WSe2 p-n junction solar cell device[124] in which laterally separated double gate electrodes were used to define the p-n semiconductor interface. Somewhat greater performance, power conversion efficiency as high as 1.5%, could be reached using WSe2/MoS2 hetero p-n junction.[128]

LEDs and transistors represent another potential application area for TMDCs applied as active materials. Similarly, to other
optoelectronic applications, the main reason for their use is lying in the direct band gap of monolayers allowing much more efficient radiative recombination of electrons and holes that produce photon than in the case of indirect bandgap semiconductors.

Light emitting transistors of WS$_2$ mono- and bilayers with ionic liquid gate (Figure 13) with ambipolar behavior were demonstrated.$^{[9]}$

Also, an electrically switchable, circularly polarized light source from p-n junctions in monolayer and multilayer tungsten diselenide (WSe$_2$) was constructed.$^{[129]}$ in which the electron–hole overlap regulated by the in-plane electric field is assumed to be responsible for the generated circularly polarized electroluminescence. Such findings are expected to pave the way for electrically switchable circularly polarized light sources and broaden the functionality of valley-optoelectronics technology.

The ambipolar conductance inherently present in WSe$_2$ monolayers, enables p-n junctions to be configured via electrostatic control. Consequently LEDs may be constructed using two local gates to define a p-n junction.$^{[121,123]}$ One major advantage of such construction is that the device relies on a single sheet of WSe$_2$. LEDs based on WSe$_2$ monolayers typically display electroluminescence efficiency between 0.1% – 1%,$^{[121,123]}$ considerably less than that of commercial organic counterparts with external quantum efficiency as high as 15–40%.

A very recent study showed that large-area flexible transparent electroluminescent screens can be achieved with monolayers of MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$ by applying an alternating voltage between the gate and the semiconductor. Due to the Schottky contacts the voltage drop is large at the interfaces of semiconductor-metal contacts, which together with the steep energy band bending results in large transient tunneling currents. The induced excess electron and hole populations that are simultaneously present during the transients recombine and produce pulsed light emission (Figure 14).$^{[130]}$
Few layered tungsten dichalcogenides, owing to their semiconducting nature, are sensitive to light irradiation. For example, our own investigation suggests that exfoliating bulk WS$_2$ powder in isopropyl alcohol can produce few layered WS$_2$ flakes; which when drop casted as thin films on pre-patterned electrodes showed ample photosensitivity (Figure 15).

Although, these flakes were found to be photosensitive, however, the performance parameters demanded of an outstanding photodetector such as photo-responsivity was found to be very low (approximately few mW A$^{-1}$) attributed to the highly disordered nature of the film. The disordered nature is also evident from the variation of photocurrent measured in the function of laser intensity (Figure 15e). Such power law dependence is common in disordered semiconductors, and attributed to mid-gap states that play a decisive role in photo-carrier relaxation. Even in its very basic exfoliated form, WS$_2$ materials were proven to be excellent candidates for devices requiring photo-switching as well as photoconduction as seen...
Figure 14. a) Schematic illustration of the tunneling transient electroluminescent device, b) optical, and electroluminescent images of a WSe$_2$ device, showing that emission of photons takes place in the proximity of the source contact edge (when an AC voltage is applied between the gate and source). Scale bar shows 10 µm. c) Electro and photoluminescence spectra of monolayer MoSe$_2$, WSe$_2$, MoS$_2$, and WS$_2$ devices. d) Band diagrams for one cycle of rectangular gate modulation (−6 to 6 V peak to peak) showing electron/hole tunneling to the semiconductor during the transients at voltage increase/decrease and subsequent relaxation with photoemission. e) Photographs of millimeter-scale transparent devices. The area of the electroluminescent surface is 3 mm × 2 mm. Reproduced with permission.[130] Copyright 2018, Springer Nature.

Figure 15. Optoelectronic properties of liquid phase exfoliated (LPE) WS$_2$ flakes. a) Tauc plot with linear extrapolation (blue line), extracted from UV–vis spectrum giving a direct band gap of ≈1.9 eV. Inset shows a dispersion of LPE WS$_2$. b) Arrhenius plot of In(conductivity) with $T^{-1}$. Inset displays the resistance variation with temperature. c) Photo current variation of a WS$_2$ device at room temperature with the red laser ($\lambda = 658$ nm, Laser power = 1 mW) ON/OFF cycling. Laser ON and OFF marked by shaded colors. d) Photo current variation under different laser power illumination (10–60 mW) for different temperatures (300–60 K). e) Photo current variation for different laser powers (plotted on a log-log scale) follows a power fit relation of $I_{ph} \propto P^\gamma$. f) 3D color plot of responsivity with the variation of laser illumination power and temperature.
in Figure 15. Excellent light matter interaction was found in several other studies including both WS2 as well as WSe2 nanomaterials. For example, multilayer WS2 phototransistor[131] was realized using the gold wire mesh method having n-type semiconductor behavior, displayed an electron mobility of 12 cm² V⁻¹ s⁻¹ as well as a photosensitive switch with an on/off ratio (defined as Iphoto/Idark) of 25. While other devices based on few-layered CVD grown WS2 films[132] and on multilayers of WS2[133] showed responsivity of 2.1 × 10⁻² mA W⁻¹ (about 3 orders of magnitude higher than exfoliated material) and 5.7 AW⁻¹, respectively. Furthermore, the latter one proved to have a fast response time of <20 ms, and external quantum efficiency of 1118%.

Several studies have also indicated the use of the liquid phase exfoliated materials in nanophotonics. Application of WS2 based materials obtained via LPE method as an effective broadband saturable absorption material was also demonstrated.[152] In this study it was shown that by integrating WS2-based saturable absorbers into a thulium-holmium co-doped fiber ring cavity stable mode-locked pulses with a temporal width of ~1.3 ps at a repetition rate of 34.8 MHz can be generated at 1941 nm. Similarly, it was also demonstrated that not only WS2 but other tungsten based materials, for example, WTe2 microflakes[153] can be utilized as a base saturable absorption material for fast mode-lockers capable of generating femtosecond pulses from fiber laser cavities. These studies indicate the importance of TMDCs in the development of passively mode locked ultrafast lasers.

Although most of these studies mainly utilize tungsten based TMDC structures, however, it is becoming clear that 2D TMDC structures, for example, WTe2 microflakes[153] can be utilized as a base saturable absorption material for fast mode-lockers capable of generating femtosecond pulses from fiber laser cavities. These studies indicate the importance of TMDCs in the development of passively mode locked ultrafast lasers.

Phototransistor relying on a single layer of WSe2[134] contacted by either Ti or Pd electrodes shed light on the importance of contact material in relation to the performance of these devices. Accordingly, WSe2 phototransistor with low Schottky-contact (Pd contact) displays excellent photo gain (1.8 × 10⁴) and detectivity (10¹⁴ jones), but with a slow response time of more than 5 s. In contrast, with high Schottky barrier Ti contacts faster response times are feasible (<23 ms), but in the expense of photo gain and detectivity. Further findings on a phototransistor built on few layers of P-WSe2 indicate the importance of electrical measurement configuration, corroborated by the considerably large photoconductivity difference observed for four-terminal configuration compared to a two terminal one. For an incident laser power of 248 nW the obtained responsivity and external quantum efficiency for two terminal configuration were found to be 18 A W⁻¹ and 4000%, respectively. This value shows response and external quantum efficiency increase of 370% when using a four terminal configuration.[135] So far, the highest responsivity value of 7 AW⁻¹ under white light illumination was reported on three atomic layers of chemical vapor transport grown WSe2 photodetectors[136] surpassing values that of graphene and transition metal dichalcogenides based heterostructures. Recent low temperature investigations of photoconductive behavior revealed considerably weak temperature dependence of responsivity suggesting that tungsten dichalcogenides may find use in photodetectors requiring temperature stability. By reducing the contact resistance and blocking the charge puddle effect through triphenylphosphine (PPh₃) and aminopropyltriethoxysilane (APTES) treatment technique the responsivity of a WSe₂ device[137] was boosted as high as 1.27 × 10⁶ A W⁻¹. Furthermore, about twofold enhancement in photoresponse time, from about 420 to 200 ms, was achieved by switching contact metal from Pt to Ti.

5.3. Chemical and Biochemical Sensors

TMDCs are sensitive to changes in their surroundings due to their high surface to volume ratio making them promising candidates for sensors. Resistive type gas sensors using WS2 nanowire-nanoflake hybrid materials as sensing elements were assessed in various redox gases (Figure 16). Since WS2...
behaves as a p-type semiconductor thus shows a positive resistance response for reducing gases (H₂S, NH₃, H₂, CO) and negative resistance response for oxidizing ones (NO). Excellent sensitivity (0.043 ppm⁻¹) and selectivity for H₂S gas was demonstrated in air buffer. As revealed by the first principle calculations and XPS analysis, the sensing mechanism for H₂S is not based on a simple analyte adsorption on and induced carrier doping in the semiconductor but because of a competitive and reversible substitution of oxygen and sulfur atoms in the lattice. Without H₂S present in the air carrier gas, S is partially replaced with O, which then substituted with S as soon as even traces of H₂S were introduced in the gas stream.[86]

Room temperature NH₃ sensing with a detection limit of 1.4 ppm was demonstrated using WS₂ thin films synthesized by reactive plasma-assisted conversion of WO₃ in the presence of H₂S.[118] Improvement of gas sensing performance on 2D WS₂ nanosheets functionalized by Ag nanowires was shown.[119] Although pristine WS₂ displayed good response to acetone and NO₂, it suffered from an incomplete recovery after NO₂ detection, which could be circumvented by the addition of Ag. Multilayer WS₂ nanoflake FET devices were studied for their photo and gas sensing behavior.[113] Photosresponsivity and external quantum efficiency of the devices during NH₃ and ethanol exposure (acting as "n-dopants") were found to increase, whereas in oxidizing atmosphere the opposite occurred.

Apart from resistive devices, also electrochemical sensors based on tungsten dichalcogenides were reported during the past few years. For instance, layered WS₂-graphene nanocomposite electrochemical sensors were proved to be suitable for the detection catechol, resorcinol and hydroquinone[140] with detection limits of 1 × 10⁻⁷ mol L⁻¹ for hydroquinone and resorcinol, and 2 × 10⁻⁷ mol L⁻¹ for catechol and recoveries of 93.6–104.8%. In another work, a sensitive electrochemical biosensor of DNA with WS₂-graphene-cithosan composite electrodes was demonstrated capable of detecting the analyte over a large dynamic concentration range from 0.01 to 500 pm with a detection limit of 0.0023 pm.[141] Furthermore, when doping single-layer WS₂ with species of high electron affinity (such as F or S) it was demonstrated capable of detecting the analyte over a large dynamic concentration range from 0.01 to 500 pm with a detection limit of 0.0023 pm. Unlike pristine WS₂, the intensity of the enhanced emission could be modulated (reduced) by exposing the doped nanoflakes to NH₃, which acts as an electron donor, with a demonstrated lowest detection limit of 1.25 ppm.[156]

Capitalizing on the strong binding affinity of WS₂ toward peptide nucleic acids (PNAs) and on its good fluorescence quenching ability for fluorophore-labeled RNA sequences, a new biosensor was developed lately with a detection limit of 0.01 pm for DNA.[142] Combination of the technique with nucleic acid amplification technique, sensors for analyzing miRNAs with a detection limit of 300 fm were shown.[143] Furthermore, the intensity of the enhanced emission could be modulated (reduced) by exposing the doped nanoflakes to NH₃, which acts as an electron donor, with a demonstrated lowest detection limit of 1.25 ppm.[156]

5.4. Catalytic, Electrocatalytic, and Energy Application

Layered transition metal sulfides are often used as catalysts by the petroleum industry in order to increase the hydrogen content of their products achieved by the hydrogenation of aromatic molecules and by the removal of contaminants. Layered transition metals are capable to catalyze hydrocarbon-upgrade reactions even when large amounts of contaminants such as sulfur, nitrogen and metals are present in the reaction. While the catalytic properties and use of layered transition metal sulfides, especially MoS₂, in catalysis can be read elsewhere,[146,147] yet surprisingly there are hardly any research publications, to the best of our knowledge, published on applying mono- to few layered tungsten dichalcogenides as the catalyst.

Instead, probably due to the great demand for new energy conversion and storage materials and technologies, the electrocatalytic activity of TMDs have been studied, in particular for the hydrogen evolution reaction to replace costly platinum group metals in the electrodes. The first demonstration of the hydrogen evolution reaction on WS₂ nanosheets obtained by a sulfurization of WO₃ nanoparticles (Figure 17) revealed only ~0.1 V overpotential of H₂ evolution in reference to Pt.[148] The promising results fostered further studies in the field to reveal any peculiarities of WS₂ nanomaterials.

As measured on chemically exfoliated 1T-WS₂ and 2H-WS₂ monolayers, the lowest overpotential and Tafel slope was observed for 1T-WS₂ catalyst, followed by the 2H phase and bulk performing only poor HER activity (Figure 18).[18] The higher activity of the 1T phase was explained by the presence of strained metallic regions in the exfoliated nanosheets thus driving the focus of future quest on 1T-WS₂ with enhanced HER activity.[149] Furthermore, triangular domains of WS₂(3–5)Se₂ monolayers grown by CVD were shown to be performing even better than plain monolayers of WS₂ or WSe₂.[150] The enhancement is proposed to be caused by the strained and thus activated basal plane of the lattice, which is otherwise rather inert.[150]

WSe₂ has also been shown to have measurable steady-state photocurrents in photoelectrochemical HER. Doping the nanoflakes with Pt further increased the activity of H₂ evolution.[151] The activity differences between metallic 1T-WS₂ and semiconducting 2H-WS₂ nanosheets in the photocatalytic hydrogen evolution reaction has also been studied.[68] Addition of 1T-WS₂ to TiO₂ increases the photoactivity more than threefold, however, at the same time addition of 2H-WS₂ decreases the photoactivity more than threefold. The reasons for the very different activities of WS₂ phases can be explained by the rapid transfer of photogenerated electron from TiO₂ to the metallic 1T phase WS₂ and reduction of a proton in the aqueous solution. Whereas in semiconducting 2H phase acts as a light harvesting
material and transfers the electron to TiO\(_2\) after photon absorption. Although, 1T-WS\(_2\) is effective co-catalyst in photocatalytic HER, it is worth pointing out that 1T-WS\(_2\)–TiO\(_2\) does not show any photoactivity under the visible light range contrary to 2H-WS\(_2\)–TiO\(_2\), which exhibits slight H\(_2\) production.

Finally, superacid-treated WS\(_2\) nanoflakes were proved to be suitable as an anode material in the Li-battery application.\(^{[48]}\) The resulted device showed three-step charge-discharge behavior, typical for binary transition metal compound-based Li-batteries. The measured first-cycle reversible electrochemical capacity, with 25 mA g\(^{-1}\) current density and voltage hysteresis of 0.93 V, was 470 mAh g\(^{-1}\), whereas after 50 cycles the capacity declined remarkably to 118 mAh g\(^{-1}\). The higher first-cycle value was speculated to be caused by intercalation of Li ions between the nanosheets.

6. Summary and Conclusive Remarks

Monolayer TMDs have recently emerged as intriguing candidates for transistor and optoelectronic devices owing to their excellent properties, such as direct band gap, chemical stability, mechanical flexibility, large in-plane carrier mobility, and photoluminescence. Although some figures may seem lower than that of graphene or ordinary semiconductors (Si, Ge, and GaAs), the application of 2D chalcogenides allow us to overcome specific shortcomings of graphene (need doping to open band gap) and conventional semiconductors (lack of mechanical flexibility and printability).

Furthermore, future optical devices could greatly benefit from the low direct band gap of monolayered TMDs that can be tuned by tensile strain or external electric field.
The progresses made in understanding the key properties of tungsten based chalcogen materials so far is incredible; however, there are several crucial aspects relevant to synthesis, structural modifications, assembly, and application developments that need to be addressed, if we want these materials to be the forerunners in technology innovations. For example, from the synthesis point of view, issues of scalability still lingers. So, one of the key research directions will be to fine tune the production processes reported so far or discover new growth strategies in order to achieve consistency in production of large quantities of high quality uniform mono-, bi-, or few-layered materials. Another open area is exploring the possibility of alloying tungsten-based chalcogens with other elements such as copper for creating ternary materials with substantially different properties, for example, tunable optical/electronic band gaps. Such alloying will also provide a simple way of creating unexplored materials having an in-plane heterostructures. The above-mentioned research direction also calls for extensive use of theoretical calculations, predictive modeling, and/or machine learning approaches to narrow down the daunting task of experimental discovery and design of these materials with advanced functionalities. Similarly, defect engineering through physical and/or chemical processes for controllably creating atomic vacancies in these materials in order to develop efficient electrocatalytic and energy materials, sensors etc. could be other directions of investigation. Tremendous opportunity also lies in assembling and investigating vertical heterostructures of layered tungsten based chalcogens with other layered structures in order to create transformative electronic/photo-electronic characteristics for device applications. At this juncture, the prospect for a variety of niche applications using tungsten based chalcogen materials looks extremely promising, however, the fruition of such proposed application will need dedicated and continual research efforts.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D tungsten chalcogenides, electrocatalysis, field-effect transistors, photodetectors, sensors

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