ABSTRACT: Metal sulﬁde and metal oxide alloys of the form Mo1−xWxS2 and Mo1−xWxO3 (0 ≤ x ≤ 1) are synthesized with varying nominal stoichiometries (x = 0, 0.25, 0.50, 0.75, and 1.0) by thermolysis of the molecular precursors MoL4 and WS(S2)L2 (where L = S2CNEt2) in tandem and in various ratios. Either transition-metal dichalcogenides or transition-metal oxides can be produced from the same pair of precursors by the choice of reaction conditions; metal sulﬁde alloys of the form Mo1−xWxS2 are produced in an argon atmosphere, while the corresponding metal oxide alloys Mo1−xWxO3 are produced in air, both under atmospheric pressure at 450 °C and for only 1 h. Changes in Raman spectra and in powder X-ray diffraction patterns are observed across the series of alloys, which conﬁrm that alloying is successful in the bulk materials. For the oxide materials, we show that the relatively complicated diffraction patterns are a result of differences in the tilt angle of MO6 octahedra within three closely related unit cell types. Alloying of Mo and W in the products is characterized at the microscale and nanoscale by scanning electron microscopy—energy-dispersive X-ray spectroscopy (EDX) and scanning transmission electron microscopy—EDX spectroscopy, respectively.

INTRODUCTION

Inorganic layered materials have attracted the attention of researchers in the last decade. Transition-metal dichalcogenides (TMDs) are of particular interest and importance because of their intrinsic 2D layered structures that are formed by bonding two chalcogen planes with a transition-metal plane. The resulting materials can be semiconducting or metallic depending on the coordination geometry of the metal centers by the chalcogen atoms in the crystal structure. For example, 2H-MoS2 (trigonal prismatic metal coordination) is a semiconductor, while 1T-MoS2 (octahedral metal coordination) is metallic. Similar to graphene, the weak van der Waals interaction between planes allows for their exfoliation as atomic layers and introduces thickness-dependent emergent properties in the 2D limit. The removal of the type MX2 (MoS2, WS2, MoSe2, and WSe2) in particular can be tuned from indirect band gap (F to Q point) to direct band gap at the K point of the Brillouin zone with increases in band gap energy due to perpendicular confinement. For example, when MoS2 is thinned down to a monolayer from the bulk, the excitonic band gap energy increases from approximately 0.85 to 1.8 eV and the quantum yield for the conduction band photoluminescence emission is dramatically increased.1−5 Hence, MoS2 and WS2 have been extensively studied,6−17 with applications including novel lubricants,18−22 electronic devices,23−26 spintronics,27−29 energy storage,30−33 sensing,34−39 catalysis,40−44 and memory storage.45−46

Novel properties can be imparted to transition-metal dichalcogenides via adding new atoms or introducing different stacking modes into their host crystal structures. For example, main group (B, P, and Cl)-doped MoS2 is a suitable candidate for gas detection and semiconductors,47,48 whereas transition-metal-doped MoS2 (Fe, Co, Ni, or Cu dopants) increases the rate of the hydrogen evolution reaction.49,50 Introduction of paramagnetic ions (Mn, Fe, Co) can potentially bestow dilute magnetic semiconducting properties amenable to spintronic applications.51−53 Heterostructures of MoS2 and TiO2 exhibit enhanced photocatalytic capability,54−56 while MoS2 and WS2...
Mo1...unequal solid-state di...crystalline host matrices. The production of ternary materials...widely researched because of their electronic, 59 band gap semiconductors (3.0 eV gas sensing;78 1 wt % MoO3 was doped into the WO3...achieve a selective detection of NH3, while the sensitivity...studied in order to produce gas sensors: MoO3 and WO3...photochromic properties. 74 produced by atmospheric chemical vapor deposition (CVD)...can be used to produce thin films of these interesting materials.

Transition-metal oxides, such as MoO3 and WO3, are wide band gap semiconductors (3.0–3.2 eV), which have also been widely researched because of their electronic...gas sensing.65–68 photocalytic,69–70 electrochromic,71–74 and photochromic properties.4–77 Various alloys have been studied in order to produce gas sensors: MoO3 and WO3 alloy thin-films produced by sol–gel methods can be used for...O2 gas sensing:78 1 wt % MoO3 was doped into the WO3 structure for NH3 and NO gas detection;79 the mixture of MoO3 (5 wt %), Au, and WO3 (94.2 wt %) was reported to achieve a selective detection of NH3, while the sensitivity...toward NO is eliminated.80 WO3/MoO3 films (7 at. % Mo) produced by atmospheric chemical vapor deposition (CVD) have been used as electrochromic devices.81 However, inhomogeneous films were reported as a challenge encountered during production.82

Traditionally, bulk transition-metal chalcogenides and oxides have been accessed either by physical vapor deposition or from solid-state reactions, respectively. Although these processes are effective at producing binary metal chalcogenides, they require high temperatures and often have extended reaction times because of the need for diffusion of atoms through solid-state crystalline host matrices. The production of ternary materials from these routes can therefore also be problematic because of unequal solid-state diffusion rates for different atoms, leading to the formation of subphases of binary materials in the final products. For oxides, this has been addressed by the introduction of sol–gel routes based on the hydrolysis of metal alkoxide precursors, while for metal chalcogenides, a range of molecular precursors have been developed, e.g., metal dithiocarbamate and metal xanthate complexes, that decompose under thermal stress to the corresponding metal sulfides. Because the mixing of precursors occurs at molecular scales and metal sulfur bonds are preformed within the complexes, the production of ternary and even quaternary materials can be achieved with excellent control of dopant homogeneity and often crystalline phase purity, and the approach can be extended to a wide range of metal chalcogenide materials.83

We have recently been interested in exploring the use of single-source precursors for the production of group VI B TMDCs. We previously reported a solventless thermolysis approach for the production of MoS2 from the decomposition of MoL4 in an inert atmosphere. Interestingly, in the same experiments, we also observed that MoL4 was decomposed under identical conditions, but in air, the corresponding metal oxide, that is, α-MoO3, was produced, leading us to the conclusion that alkyl dithiocarbamato molybdenum(IV) complexes could act as “masked” precursors toward oxides as well as chalcogenide materials with low processing temperatures (<500 °C) and comparatively short reaction times (~1 h).84 We have also shown, subsequently, that MoL4 can be chemically decomposed to produce nanocrystalline MoS2 at room temperature at the liquid–liquid interface.85 We therefore hypothesized that through a dual precursor reaction of MoL4 and a structurally similar tungsten precursor, WS(S2)L2, we could also potentially access a range of layered ternary metal chalcogenide alloys of the form Mo1−xWxO3 (0 ≤ x ≤ 1) as well as produce the family of Mo1−x,WxS2 as...rate data combined with electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). This approach represents a step change in producing ternary transition-metal dichalcogenide alloys at a fraction of the time compared to traditional solid-state reactions and with control of alloying achieved at the nanoscale.

**EXPERIMENTAL SECTION**

**General Considerations.** All materials were purchased from Sigma, Merck, or Fisher and used without purification.

**Synthesis of Tetrakis(diethylthiocarbamato)molybdenum(IV) (MoL4).** The title complex was synthesized following the method reported previously by Decoster et al.86 Molybdenum hexacarbonyl (1.0 g, 3.8 mmol) and tetraethylthiuram disulfide (2.2 g, 7.6 mmol) were mixed in degassed acetone (30 mL), and the mixture was heated at 80 °C under reflux for 2 h. The reaction was cooled to room temperature and a black microcrystalline precipitate formed, which was collected by vacuum filtration. The solid collected was washed three times with pentane (3 × 30 mL). The final product was dried overnight in a vacuum oven. Anal. Calcd for MoL4 (%): C, 34.86; H, 5.85; N, 8.13. Found (%): C, 34.49; H, 5.65; N, 7.93.
The title complex was synthesized using the method reported by Lewis et al. Ammonium tetramethylmolybdate (2.9 g, 8.4 mmol) and sodium diethylthiocarbamate (7.6 g, 34 mmol) were mixed in deionized water (300 mL) and diluted HCl (2 M) was added dropwise until the pH of the solution reached ca. 2. The dark green precipitate which formed was collected by vacuum filtration and was washed three times with deionized water (3 × 100 mL). The crude product was dried in a vacuum oven for 1 h and left to cool down to room temperature before being drop-cast onto a standard (284.8 eV), whose binding energy relates to the surface chemistry of the sample. 

Synthesis of Bulk Solid-State Alloys Mo$_1$-$x$W$_x$S$_2$ and Mo$_1$-$x$W$_x$O$_3$. A mixture of precursors MoL$_4$ and WS(S$_2$)L$_2$ powders in various ratios (x = 0, 0.25, 0.50, 0.75, and 1.0) was heated to 500 °C in air for 1 h, followed by cooling to room temperature, and the solid products were then collected. For oxides, the mixture was heated to 500 °C in air for 1 h, following by cooling to room temperature, and the solid products were then collected.

Synthesis of Nanoscale Mo$_1$-$x$W$_x$S$_2$ and Mo$_1$-$x$W$_x$O$_3$. A mixture of precursors MoL$_4$ and WS(S$_2$)L$_2$ powders in various ratios (x = 0, 0.25, 0.50, 0.75, and 1) were dissolved in ethanol/water (50/50) and sonicated for 20 min using an ultrasonic bath (30 W/37 Hz), followed by centrifugation at 1500 rpm for 45 min to remove bulk materials. The supernatants were resuspended in deionized water and were further centrifuged at 12,000 rpm for 45 min. The precipitates after 12,000 rpm were collected and diluted in deionized water before being drop-cast onto SiO$_2$/Si substrates or transmission electron microscopy (TEM) grids for further characterization.

Material Characterization. Raman spectroscopy was performed in HORIBA LabRaman Evolution HR, with a 488 nm excitation wavelength laser (2.5% ND filter, acquisition time 120 s, accumulation 2). The silicon peak was calibrated to 520 cm$^{-1}$ as a reference. Powder X-ray diffraction (PXRD) measurements were conducted on a PANalytical X'Pert Pro, which has a θ/2θ geometry with a copper line focus X-ray tube (Kα = 1.5406 Å). Zero background sample holders were used for all the samples to reduce noise. XPS was performed using a Thermo Scientific Kratos Axis Ultra Hybrid system equipped with a monochromatic Al Kα anode (150 W) equipped with a charge neutralizer. CasaXPS software was used for data analysis and curve fitting, with all peaks charge-corrected via fitting the C 1s peak to a standard (284.8 eV), whose binding energy relates to the surface adventitious carbon. To analyze the oxidation state and surface chemical composition of the compounds, a library (Kratos) was employed for relative sensitivity factors and the peaks were fitted with 70% Gaussian and 30% Lorentzian. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were run on a Zeiss Sigma VP FEG-SEM (SE) with accelerating voltages of 1−1.5 and 30 kV, respectively. High-resolution TEM (HRTEM) and scanning TEM (STEM) with EDX were performed using either a Talos F200X (200 kV, FEG) microscope equipped with a Super-X EDS detector and fitted with a fast-acquisition 4k CMOS camera or an FEI Tecnai F30 (300 kV, FEG) fitted with an Oxford Instruments X-Max 80 silicon drift detector (SDD) EDX detector and T20 (200 kV, LaB 6) equipped with an Oxford Instruments X-Max3 80TLE SDD or a probe side aberration-corrected FEI Titan G2 ChemiSTEM (200 kV, FEG) with a beam current of 15−30 nA. EDX spectra and surface images were processed using OI Aztec or Bruker ESPRIT software. Atomic force microscopy (AFM) was performed using a Bruker MultiMode 8 microscope in ScanAsyst mode for automatic image optimization. SiO$_2$/Si substrates were used (lateral size 8 × 8 mm). Elemental analysis was conducted by the microanalytical laboratory at the University of Manchester using a Thermo Scientific Flash 2000 organic elemental analyzer.

RESULTS AND DISCUSSION

We reasoned that by using mixtures of group VI B metal dithiocarbamate complexes in tandem, we could produce either metal sulfide or metal oxide materials of the form Mo$_1$-$x$W$_x$S$_2$ or Mo$_1$-$x$W$_x$O$_3$ where ratios of the precursors were chosen so that nominally x = 0, 0.25, 0.50, 0.75, or 1.0. The molecular precursors MoL$_4$ and WS(S$_2$)L$_2$ (Scheme 1) have been previously used to produce Mo$_1$-$x$W$_x$S$_2$ by AACVD, and for this study, these precursors were produced via the methods reported by Lewis et al. These precursors have similar thermal profiles and codecompose in the solid state to give alloyed materials, which was previously shown by Lewis et al. to produce the target metal chalcogenide alloys in AACVD experiments to produce thin films. Here, a mixture of both precursors in the desired mole fraction of W (i.e., x) was heated at a relatively low temperature (450 or 500 °C) in a tube furnace for 1 h under either an argon flow atmosphere (for sulfides) or in air (for oxides). The metal chalcogenide and oxide alloys produced as crystalline powders from these short (1 h) thermolysis reactions were studied using a range of characterization techniques.

Structural Analysis of Mo$_1$-$x$W$_x$S$_2$ and Mo$_1$-$x$W$_x$O$_3$ Alloys. PXRD was performed to structurally characterize the materials. The PXRD patterns of pristine MoS$_2$, WS$_2$, and their sulfide and oxde alloys are shown in Figure 1. We first
consider the materials produced in an argon atmosphere. The almost identical lattice constants of MoS2 and WS2 result in an overlapping of diffraction peaks. The diffraction peak at $2\theta \sim 33.5^\circ$ can be ascribed to the (100) and (101) planes and $2\theta \sim 59^\circ$ corresponds to the (110) plane of 2H-MoS2 (JCPDF no. 37-1492) and 2H-WS2 (JCPDS card no. 84-1398). For the alloys, Mo1-xWxS2, no significant change is observed in these patterns upon alloying except that a minor peak becomes noticeable at about 70° as the level of W increases to 75%, which corresponds to the (200) plane. For pure WS2, a small peak appears at $2\theta \sim 23.5^\circ$, which might be caused by oxidation. Almost no diffraction from the (002) planes ($2\theta \sim 15^\circ$) is observed, which is an indication of the ultrathin nature of the alloyed materials formed. Indeed, the pattern we observe with these systematic absences of the usually intense (00l) reflections is remarkably similar to that of single-layer MoS2.89 In addition, the peaks are relatively broad, which suggests that the materials are also nanoscale in their $ab$ plane, and this is a feature that is observed for every Mo–W sulfide alloy investigated.

For materials derived from the decomposition of WS(S2)L2 in air at 500 °C, only the diffraction pattern for monoclinic WO3 is observed (JCPDF card no. 43-1035). The crystal structure of tungsten trioxide is temperature-dependent, adopting a tetragonal structure at temperatures above 740 °C, orthorhombic from 330 to 740 °C, monoclinic from 17 to 330 °C, triclinic from −50 to 17 °C, and monoclinic again at temperatures below −50 °C. Therefore, in this case, we conclude that the most thermodynamically stable structure at room temperature is adopted in the product of decomposition,90,91 although we do note that triclinic WO3 is the most thermodynamically stable polymorph overall.92 Similarly, for materials derived from the decomposition of MoS(S2)L2 in air at 500 °C, only the diffraction pattern for orthorhombic MoO3 is observed (JCPDF card no. 05-0508).

In contrast to the WO3 and MoO3 end compounds, which are single phases, the Mo1-xWxO3 alloys produced adopt a range of interrelated crystalline structures. With 25 and 50% Mo doping in WO3, we observed the emergence of new peaks for the (120) and (112) Bragg planes, with peaks shifted from 24.1 to 25.2° (marked “*” in Figure 1b). This is caused by another phase of WO3 and it is known that mixtures of phases can potentially be formed during alloying of this system, which we explore later.92-97 A summary of the shifts in the $2\theta$ peak position of individual Bragg planes as a function of the Mo mole fraction in Mo1-xWxO3 alloys using the Miller indices previously designated by Stevenson and co-workers98 is presented in Figure S6 (Supporting Information). The vanishing (020) reflection among the cluster of three peaks around 23° is a result of Mo doping into WO3,99 this is due to preferred orientation in the (00l) planes with respect to the (0k0) planes.100,101 Hence, for this quite complicated metal oxide system, we employed Rietveld refinement of the diffraction data to identify and quantify the constituent crystalline phases. Refinement of the diffraction data for Mo1-xWxO3 ($0.25 \leq x \leq 0.75$) reveals that in all cases the alloys comprise three highly related WO3 structures: orthorhombic, monoclinic, and triclinic WO3, which in all cases is accompanied by a varying amount of α-MoO3. The variations in the crystal structure away from the parent monoclinic WO3 structure are strain-induced; as the amount of Mo is reduced, the amount of monoclinic structure is increased. Hence, from this analysis, we may conclude that the system is therefore best described as a paracrystal with varying short to medium local order in the WO3 phase, leading to highly related crystal systems that can be envisaged as being structurally related by varying the tilt in MoOx octahedra ($M = Mo$ or $W$), where the local variation in the $M=O$ tilt angle and thus crystal structure adopted is governed by the amount of Mo dopant (Figure 2).

Figure 2. Structures of crystalline phases of Mo1-xWxO3 (0.25 ≤ x ≤ 0.75) produced in decomposition reactions determined by Rietveld refinement of PXRD data: (a) orthorhombic Mo1-xWxO3; (b) monoclinic Mo1-xWxO3; and (c) triclinic Mo1-xWxO3, accompanied by views of Mo6 octahedra (where $M = Mo$ or $W$) in the unit cells of (d) orthorhombic Mo1-xWxO3; (e) monoclinic Mo1-xWxO3; and (f) triclinic Mo1-xWxO3. All three systems share similar unit cell parameters and are related in simple terms by variation in strain-induced tilting of Mo6 octahedra caused by doping of Mo into the structure.
Figure 3. Raman spectra of Mo$_{1-x}$W$_x$S$_2$ and Mo$_{1-x}$W$_x$O$_3$ at various nominal mole fractions of W ($x = 0, 0.25, 0.5, 0.75, \text{and } 1$). (a) MoS$_2$–WS$_2$ alloys in comparison with MoS$_2$ and WS$_2$; (b) MoO$_3$–WO$_3$ alloys in comparison with MoO$_3$ and WO$_3$. (c) Raman shifts of the A$_{1g}$ (MoS$_2$/WS$_2$), E$_{2g}$ (MoS$_2$) and E$_{2g}'$ (WS$_2$) phonons observed for Mo$_{1-x}$W$_x$S$_2$ ($x = 0, 0.25, 0.50, 0.75 \text{ and } 1$). (d) Raman shifts of O=W–O stretching and bending modes (WO$_3$). All spectra were acquired using a 488 nm laser as the excitation source. The Raman spectra presented here for MoS$_2$ and α-MoO$_3$ are included for comparison and are previously reported by Lewis et al. "Direct synthesis of MoS$_2$ or MoO$_3$ via Thermolysis of a Dialkyl Dithiocarbamato Molybdenum(IV) Complex". Chem. Commun. 2019, 55, 99–102, which is licensed under a Creative Commons Attribution 3.0 Unported Licence (CC-BY 3.0, https://creativecommons.org/licenses/by/3.0/) and is published by the Royal Society of Chemistry. $^{14}$

produced. $^{107}$ Ghiotti and co-workers produced five stoichiometry-dependent phases from a sol–gel processing route to Mo$_{1-x}$WO$_3$ where the phases observed seem to be dependent on the stoichiometry of the material produced, with one stoichiometry ($x = 0.2$) showing predominantly mixed phase products. $^{104}$ Hibble and Dickens reported the synthesis of Mo$_{1-x}$WO$_3$ with various stoichiometries from three various routes (sol–gel, solid-state reaction, and co-crystallization); yet, only single phase products were produced, which adopted the monoclinic and the $\zeta$ structures, $^{84}$ the latter described by Salje et al. $^{95}$ Similarly, Figlarz et al. produced Mo$_{1-x}$WO$_3$ alloys with the hexagonal ($x < 0.2$), orthorhombic ($0.2 < x < 0.6$), and cubic ReO$_3$ ($0.6 < x < 1.0$) structures. $^{105}$ Stevenson and co-workers have noted that the initial stoichiometry of the material may have a major influence over which phases are formed as final products after sintering is performed. $^{106}$ In the context of the solid-state reactions described in this paper, it seems that because we are rapidly producing the alloys that we trap out most of the possible phases as metastable products as in all cases for the Mo$_{1-x}$WO$_3$ alloys we see a range of interrelated phases produced.

Raman analysis provides complementary structural information to diffraction methods. Raman spectra of MoS$_2$ and WS$_2$ (i.e., $x = 0, x = 1$) have two signature optical phonon modes: the in-plane optical mode ($E_{2g}$) and the out-of-plane optical mode ($A_{1g}$) (Figure 3a). Accordingly, intense peaks are observed for the MoS$_2$ ($x = 0$) sample at 381 and at 403 cm$^{-1}$, which we attribute to the $E_{2g}$ in-plane and the $A_{1g}$ out-of-plane vibrational mode, respectively. The difference between both peaks has previously been reported to be indicative of layer number ($\Delta \nu = 18$ cm$^{-1}$ for monolayer, $\Delta \nu = 21$ cm$^{-1}$ for bilayer molybdenum disulfide). $^{110,112}$ For the MoO$_3$ sample, the $E_{2g}'$ peak appears at $382 \text{ cm}^{-1}$ and the $A_{1g}$ mode is centered at $404 \text{ cm}^{-1}$ ($\Delta \nu = 22$ cm$^{-1}$), with the peak corresponding to the silicon substrate located at $520 \text{ cm}^{-1}$. $^{113}$ For Mo$_{0.70}$W$_{0.25}$S$_2$, both the $E_{2g}$ and $A_{1g}$ phonons appear at positions similar to MoS$_2$ (381 and 404 cm$^{-1}$). However, when the amount of tungsten in the sample is increased (mol % Mo is reduced) in Mo$_{0.50}$W$_{0.50}$S$_2$ the $E_{2g}$ shifts from $\sim 381$ to $378 \text{ cm}^{-1}$ and the $A_{1g}$ remains at $403 \text{ cm}^{-1}$ (Figure 3c). By further increasing the tungsten content in the Mo$_{0.25}$W$_{0.75}$S$_2$, the $E_{2g}$ phonon softens and is further shifted to $375 \text{ cm}^{-1}$, while the $A_{1g}$ phonon is blue-shifted ($403–408 \text{ cm}^{-1}$) and a new peak appears at $350 \text{ cm}^{-1}$, which is characteristic of WS$_2$. $^{112}$ For the WS$_2$ sample (i.e., $x = 1.0$), the Raman spectrum includes the longitudinal acoustic mode [LA(M)] located at $171 \text{ cm}^{-1}$, with the $E_{2g}$ and $A_{1g}$ phonon modes observed at $353$ and $414 \text{ cm}^{-1}$, respectively (Figure 2a). The difference in the peak maxima wavenumbers ($\Delta \nu = 61 \text{ cm}^{-1}$) indicates that WS$_2$ could potentially be on average somewhere between a bilayer and a few layers in thickness ($\Delta \nu = 60 \text{ cm}^{-1}$ for monolayer and $65 \text{ cm}^{-1}$ for bulk), $^{114–116}$ This is also evidenced by the appearance of the 2LA(M) mode, which is reported to monotonically increase in intensity as a function of decreasing layer number. $^{117}$

The Raman spectra of Mo$_{1-x}$W$_x$O$_3$ samples also give insight into their structure and bonding. All spectra recorded have two clear peaks that correspond to the vibrational modes of WO$_3$ with some noticeable minor peaks below $100 \text{ cm}^{-1}$, which also appear in pristine WO$_3$ (Figure 3b). For undoped WO$_3$, two sharp peaks are located at $354$ and $416 \text{ cm}^{-1}$, indicating that the WO$_3$ is highly crystalline. $^{118,119}$ Additionally, two broad peaks located at $704$ and $804 \text{ cm}^{-1}$ can both be assigned to O=W–O stretching vibration modes, $^{120,121}$ with the latter arising from doubly bound corner shared octahedra in the structure. These modes are the strongest signals among all the phonon modes observed and are upshifted ($713 \rightarrow 718$ and $810 \rightarrow 819 \text{ cm}^{-1}$) upon increasing at. % of Mo in the alloys. The increase of peak intensities of the O=W–O stretching mode relative to the other peaks is concomitant with the increase of Mo dopant atoms in the WO$_3$ structure. This has previously been ascribed
to both the shorter length of the Mo–O bond compared to the W–O bond, and in our case it is potentially due to variation in strain between related crystallographic species as revealed by our Rietveld analysis (vide supra). For all alloys, no peaks in the range of 350–420 cm$^{-1}$ were observed, which suggests that the structures of doped alloys are different from that of pristine WO$_3$. New peaks appear at 271–275 and 328–331 cm$^{-1}$ and can be assigned to O–W–O bending modes. However, peak shifts from 271 → 275, 328 → 331, 713 → 718, and 810 → 819 cm$^{-1}$ (Figure 3d) may be caused by the phase transition of WO$_3$. A higher wavenumber of this Raman stretching mode could indicate a more distorted structure; similar shifts associated with phase transitions from orthorhombic (Pnma) to monoclinic (P2$_1$/n) structures in WO$_3$ have been reported. Hence, the various phases that were determined from refinement of X-ray diffraction (XRD) data (vide supra) in this system could be the main reason for these observed peaks’ shifts. This is also supported by the new peak that appears at 319 cm$^{-1}$ in the Mo$_{0.6}$W$_{0.4}$O$_3$ alloy, which indicates that the lattice incorporation has affected this molecular vibration mode. For MoO$_3$, the vibrational modes for Mo chains are located at 112, 125, and 154 cm$^{-1}$, and the oxygen wagging modes are observed as peaks at 281 and 288 cm$^{-1}$ (B$_{2g}$, B$_{3g}$). The symmetric and asymmetric stretching vibrational phonon modes located at 664 cm$^{-1}$ (B$_{2g}$, A$_g$), 816 cm$^{-1}$ (A$_g$, B$_{1g}$), and 993 cm$^{-1}$ (A$_g$, B$_{1g}$) are characteristic peaks of \( \alpha \)-MoO$_3$. Overall, the Raman results indicate that alloying has been achieved with a predominant crystalline structure of MoS$_2$ in the sulfide alloys, while the WO$_3$ structure is primarily adopted in the oxide alloys within the reported concentration range.

**Elemental Analysis of Alloying in Mo$_{1-x}$W$_x$S$_2$ and Mo$_{1-x}$W$_x$O$_3$ in the Bulk and at the Surface.** XPS was performed to measure elements at the surface upon doping. High-resolution measurements of Mo 3d and W 4d peaks were run in one scan in order to minimize charging effects. Atomic concentrations derived from XPS were plotted as a function of the nominal concentrations for Mo and W individually (Figure 4e). The ratios of Mo$^{4+}$ or W$^{4+}$ to S 2s are very close to 1:2 with the full width at half-maximum (fwhm) range $\sim 1.3–1.5$ (±0.2) eV. The high-resolution scan for sulfides in Figure 4a shows that the fitted Mo$^{6+}$ (surface oxidation) binding energies appear at 233.5 eV (Mo 3d$_{5/2}$), while Mo$^{6+}$ (MoS$_2$) is located in the range of 230.4–230.7 eV (Mo 3d$_{5/2}$) with S 2s peaks at around 227.7–228.3 eV. Diminishing of peaks for Mo$^{6+}$ and Mo$^{5+}$ occurs as the level of W doping increases. When W

Figure 4. Quantification of elements at the surface and in bulk. XPS spectra: (a,c) Mo 3d region and (b,d) W 4d region for Mo$_{1-x}$W$_x$S$_2$ and Mo$_{1-x}$W$_x$O$_3$ alloys in various mixture concentrations (x = 0, 0.25, 0.5, 0.75, and 1). Comparison of nominal at. % of the Mo atom and the Mo at. % found in quantification by (e) XPS and (f) SEM–EDX spectroscopy.
content increases to 75%, a peak for the Mo^{6+} binding energy disappears along with a noticeable decrease of peak intensity for Mo^{4+}. The binding energy for Mo^{4+} 3d_{5/2} also shifts from 230.7 to 230.4 eV. This effect is potentially caused by the reduced electron attraction provided by S and increased electron attraction by W due to the increase in electronegativity and orbital radii with the increase of W dopant.\(^{127-129}\) Both the Mo^{4+} and S 2s peaks present a noticeable intensity difference arising from the W substitution, as the fwhm for Mo^{4+} changes from 1.1 to 0.88 to 1.3 eV and fwhm for S 2s changes from 3.11 to 2.57 and to 2.78 eV. The sharpening of both peaks for Mo_{0.5}W_{0.5}S_{2} indicates a higher binding energy for this composition. Figure 4b presents the binding energies for the tungsten doublet peak W 4d_{5/2} changing from 247.5 to 246.7 and to 245.7 eV, which could be assigned to W^{4+} ions in WS_{2}.\(^{13}\) The binding energies for S 2p are located at about 163.5 eV for all the sulfide alloys.

The majority of oxide alloys show only one clear Mo oxidation state; the observed peaks for Mo 3d_{5/2} located at 233.0–233.2 eV can be attributed to Mo^{6+} in MoO_{3} (Figure 4c). Only minor peaks for Mo^{3+} are shown in the Mo_{0.5}W_{0.5}O_{3} alloy; the insignificant intensities indicate a relatively pure oxide state for samples in all the ratios. The binding energies are in good agreement with that in the literature.\(^{130,131}\) While the W 4d_{5/2} and W 4d_{3/2} peaks are at around 248 and 260 eV, respectively (Figure 4d), a peak difference of \(\sim 12\) eV was observed which we attribute to the spin–orbit splitting, suggesting the existence of W^{6+} (WO_{3}).\(^{132}\)

The nominal at. % of the Mo atom is compared with elemental analysis by XPS and SEM–EDX (Figure 4e,f). All the methods show an increase in dopant at. % that gave approximately linear fittings (\(R^2 \geq 0.88–0.98\)) when increasing the nominal dopant percentage (at. % Mo). Peak fitting of the XPS spectra show that the samples are relatively more Mo-rich than the simple nominal stoichiometry would suggest within the depth sampled, while integration of SEM–EDX emission generally agrees with the elemental concentration defined by the precursor mixture. The discrepancy between XPS and

Figure 5. Investigation of sample morphology and elemental distribution in Mo_{1-x}W_{x}S_{2} and Mo_{1-x}W_{x}O_{3} at the microscale. (a) Secondary electron SEM images showing the surface morphology of Mo_{1-x}W_{x}S_{2} and Mo_{1-x}W_{x}O_{3} alloys. SEM images for pristine MoS_{2} and MoO_{3} were obtained using samples from a previous report.\(^{64,65}\) SEM images for pristine MoS_{2} and MoO_{3} before doping were also presented here for morphological comparison; (b) SEM–EDX spectrum maps of Mo_{1-x}W_{x}S_{2} and Mo_{1-x}W_{x}O_{3} showing apparently homogeneous spatial distributions of S, Mo, W, and O atoms in alloys. In the oxides, carbon is also mapped (no S detectable). Scale bars in (b) = 20 \(\mu\)m.

Figure 6. TEM characterization of Mo_{1-x}W_{x}S_{2} and Mo_{1-x}W_{x}O_{3} alloys. (a–f) TEM images of sulfides and oxides, (a) Mo_{0.75}W_{0.25}S_{2}, (b) Mo_{0.5}W_{0.5}S_{2}, (c) Mo_{0.25}W_{0.75}S_{2}, (d) Mo_{0.75}W_{0.25}O_{3}, (e) Mo_{0.5}W_{0.5}O_{3}, (f) Mo_{0.25}W_{0.75}O_{3}. The highlighted orange circles on the right-hand side on the oxide alloys column indicate the outline of nanoparticles. (g) Size distribution histograms showing the diameter of nanoparticles, with sizes ranging between 2 and 9 nm for all the alloys. (h) Histograms showing lateral size distribution of nanosheets for sulfide alloys’ ranging from 3 to 19 nm.
SEM−EDX spectroscopy is due to the depths pro
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led; for XPS, this is around 6 nm and hence these quanti
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ect the chemical composition found at the surface of the
material, while SEM−EDX spectra arise from emission of
photons from within the bulk of the sample and the sampling
depth is dependent on beam voltage.

Analysis of Alloying in Mo1−xWxS2 and Mo1−xWxO3 at
the Microscale. Inspection of surface morphology was
conducted by SEM in the secondary electron imaging mode.
We have previously reported MoS2 as nanostructured
powders. After doping, a similar fine scale surface
morphology was observed for all the Mo1−xWxS2 alloys (Figure
5a), which is consistent with few-layer MoS2 reported
previously. The Mo0.5W0.5S2 and Mo0.25W0.75S2 alloys are
observed to be particularly smooth, suggesting a uniform,
nanoscale structure. The lateral size for features visible in the
SEM images of the doped oxides are all larger: ca. 100 nm in
Mo0.3W0.7O3, ca. 300 nm in Mo0.25W0.75O3 and ca. 1 μm in
Mo0.75W0.25O3. The morphology also changes from more
equiaxed structures at high W concentrations to platelet
structures formed with increasing Mo content. SEM−EDX
spectroscopy mapping shows that the elements are evenly
distributed in all the alloys at the microscale (Figure 5b).

Analysis of Alloying in Mo1−xWxS2 and Mo1−xWxO3 at
the Nanoscale. We were interested in studying the elemental
distributions at the nanometer scale in order to fully
demonstrate alloying over a range of length scales. We used
ultrasonication in water/ethanol and centrifugation to produce
nanoscale materials. TEM was used to study the nanoscale
particle morphology (Figure 6a−f) and crystallinity of the
samples (Figure S2). Interestingly the sulphide alloys all
contained both small particles and nanosheets with size
distributions shown in Figure 6g,h. Tilt experiments con
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rmed
that these were indeed separate populations. The nanoparticles
have diameters peaked around 4−5 nm and size distributions
in the range of 3−9 nm, while nanosheets are typically larger
laterally, in the range 5−17 nm, but with typical thicknesses of
less than three atomic layers. The presence of both nanosheets
and nanoparticles is consistent with the X-ray data collected
and the van der Waals layered structures of the group VI B
sulphides, with both types of morphology having been previously
reported for MoS2. TEM investigation of the alloyed oxides showed them to
consist of roughly spherical nanoparticles with mean sizes of
between 3 and 5 nm. These simple 0D structures are
consistent with the WO3 crystal structure, which is less
anisotropic than the sulphides. A few larger nanoparticles >10
nm were also observed in the oxide sample and these showed
some evidence of surface faceting, as is expected for surface
energy minimization in larger crystals (see Figure S3). AFM
was also applied to investigate the morphology of the alloyed
sulphide and oxide nanomaterials, giving results that are broadly

![Figure 7. Study of elemental composition and spatial distribution of elements in Mo1−xWxS2 and Mo1−xWxO3 at the nanoscale using electron microscopy in combination with emission spectroscopy. (a−f). HAADF-STEM and STEM−EDX mapping of spatially resolved Mo, W, S, and O for Mo1−xWxS2 and Mo1−xWxO3 alloys within different ratios (x = 0.25, 0.5, and 0.75). The resulting elemental maps indicate approximately uniform distributions of the elements over this length scale. Scale bar = 5 nm. (g) Atomic resolution HAADF-STEM image for Mo0.5W0.5S2 showing contrast difference caused by dopant atoms (z contrast). The line scan reveals atomic columns that are expected to be richer in W or Mo atoms, respectively, consistent with alloying at the atomic scale.](image-url)
consistent with TEM size analysis. However, the ultrasmall size of the nanoparticles and their tendency to form aggregates make quantitative interpretation of such data difficult (Figure S1a,b).

High-angle annular dark-field (HAADF) STEM and STEM−EDX was carried out in order to use nanoscale elemental mapping to confirm the composition and elemental homogeneity of the alloyed nanomaterials (Figure 7a−f). HAADF-STEM images showed aggregated clusters of Mo$_{1-x}$W$_x$S$_2$ nanosheets and Mo$_{1-x}$W$_x$O$_3$ nanoparticles. STEM−EDX spectrum imaging revealed a fairly even distribution of the constituent elements Mo, W, S, and O at the nanometer scale (Figure 7a−f), supporting the successful alloying of these nanoscale materials. The sensitivity of these samples to damage by the high-energy STEM electron probe prevents their compositional analysis at the atomic scale. Nonetheless, we can exploit the atomic number sensitivity of the HAADF-STEM imaging mode to probe local compositional difference, and no large differences were observed. In nanoparticles and thicker nanosheets, this is to be expected as atomic scale compositional differences are averaged along the electron beam direction. However, in the few-layer sulfides viewed along [001], there are only a few atoms superimposed and the large variability in HAADF intensity we observe for neighboring atomic columns suggest that Mo and W are alloyed at the atomic scale (Figure 7g). As limited information on alloying can be extracted from diffraction data on the sulfide materials, line profiles were extracted through STEM−EDS elemental maps (Figure 8). These demonstrate uniform alloying in the samples at the nanoscale, with quantification at the expected level based on the Cliff Lorimer absorption corrected Mo/W composition ratio.

**CONCLUSIONS**

We have shown that both Mo$_{1-x}$W$_x$S$_2$ and Mo$_{1-x}$W$_x$O$_3$ alloys can be produced via a rapid, low-temperature molecular precursor method. Control of alloying is readily achieved with resulting variations in morphological and crystallographic changes as demonstrated by Raman spectroscopy, XRD, SEM−EDX, and TEM. The sulfide Mo$_{1-x}$W$_x$S$_2$ alloys generally all adopt the MoS$_2$ structure with 2H-hexagonal layered polytype. In the Mo$_{1-x}$W$_x$O$_3$ oxides, the WO$_3$ and MoO$_3$ structures are dominant; however, for alloys midway between the end compounds (i.e., 0.25 ≤ x ≤ 0.75), the picture is complicated and Rietveld refinement reveals that a series of structurally related unit cells (orthorhombic, triclinic, and monoclinic WO$_3$ and orthorhombic MoO$_3$) exist for these materials that are related by tilt in MO$_6$ octahedra induced by strain introduced by Mo doping and hence we conclude that these solids possess a high degree of local disorder and may be better considered as paracrystalline materials. For all alloys, we reveal that the doping of materials is coherent across a range of length scales covering 6 orders of magnitude. The new synthetic pathway that we present here allows simple access to these interesting alloy materials at relatively low temperatures and with excellent control of elemental composition and access to potentially interesting metastable structures.
REFERENCES

(1) Zhang, Y.; Chang, T.-R.; Zhou, B.; Cui, Y.-T.; Yan, H.; Liu, Z.; Schmitt, F.; Lee, J.; Moore, R.; Chen, Y.; Lin, H.; Jeng, H.-T.; Mo, S.-K.; Hussain, Z.; Bansil, A.; Shen, Z.-X. Direct observation of the transition from indirect to direct bandgap in atomically thin epitaxial MoSe₂. Nat. Nanotechnol. 2014, 9, 111–115.

(2) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically thin MoS₂: a new direct-gap semiconductor. Phys. Rev. Lett. 2010, 105, 136805.

(3) Tongay, S.; Zhou, J.; Ataca, C.; Lo, K.; Matthews, T. S.; Li, J.; Grossman, J. C.; Wu, J. Thermally driven crossover from indirect toward direct bandgap in 2D semiconductors: MoSe₂ versus MoS₂. Nano Lett. 2012, 12, 5576–5580.

(4) Ellis, J. K.; Lucero, M. J.; Scuseria, G. E. The indirect to direct band gap transition in multilayered MoSe₂ as predicted by screened hybrid density functional theory. Appl. Phys. Lett. 2011, 99, 261908.

(5) Kumar, A.; Ahluwalia, P. Electronic structure of transition metal dichalcogenides monolayers 1H-MX₂ (M= Mo, W; X= S, Se, Te) from ab-initio theory: new direct band gap semiconductors. Eur. Phys. J. B 2012, 85, 186.

(6) Hong, X.; Kim, J.; Shi, S.-F.; Zhang, Y.; Jin, C.; Sun, Y.; Tongay, S.; Wu, J.; Zhang, Y.; Wang, F. Ultrafast charge transfer in atomically thin MoS₂/WS₂ heterostructures. Nat. Nanotechnol. 2014, 9, 682–686.

(7) Duan, X.; Wang, C.; Shaw, J. C.; Cheng, R.; Chen, Y.; Li, H.; Wu, X.; Tang, Y.; Zhang, Q.; Pan, A.; Jiang, J.; Huang, Y.; Duan, X. Lateral epitaxial growth of two-dimensional layered semiconductor heterojunctions. Nat. Nanotechnol. 2014, 9, 1024–1030.

(8) Tongay, S.; Fan, W.; Kang, J.; Park, J.; Koldemir, U.; Suh, J.; Narang, D. S.; Liu, K.; Ji, J.; Li, J.; Sinclair, R.; Wu, J. Tuning interlayer coupling in large-area heterostructures with CVD-grown MoS₂ and WS₂ monolayers. Nano Lett. 2014, 14, 3185–3190.

(9) Huo, N.; Kang, J.; Wei, Z.; Li, S.-S.; Li, J.; Wei, S.-H. Novel and enhanced optoelectronic performances of multilayer MoS₂–WS₂ heterostructure transistors. Adv. Funct. Mater. 2014, 24, 7025–7031.

(10) Zhang, X.-Q.; Lin, C.-H.; Tseng, Y.-W.; Huang, K.-H.; Lee, Y.-H. Synthesis of lateral heterostructures of semiconducting atomic layers. Nano Lett. 2014, 15, 410–415.

(11) Liang, L.; Meunier, V. First-principles Raman spectra of MoS₂, WS₂, and their heterostructures. Nanoscale 2014, 6, 5394–5401.

(12) Chen, K.; Wan, X.; Wen, J.; Xie, W.; Kang, Z.; Zeng, X.; Chen, H.; Xu, J.-B. Electronic properties of MoS₂–WS₂ heterostructures synthesized with two-step lateral epitaxial strategy. ACS Nano 2015, 9, 9868–9876.

(13) Zhang, Z.; Chen, P.; Duan, X.; Zang, K.; Luo, J.; Duan, X. Robust epitaxial growth of two-dimensional heterostructures, multiheterostructures, and superlattices. Science 2017, 357, 788–792.

(14) Chen, K.; Wan, X.; Xie, W.; Wen, J.; Kang, Z.; Zeng, X.; Chen, H.; Xu, J. Lateral Built-In Potential of Monolayer MoS₂–WS₂ In-Plane Heterostructures by a Shortcut Growth Strategy. Adv. Mater. 2015, 27, 6431–6437.

(15) Zhang, J.; Wang, J.; Chen, P.; Sun, Y.; Wu, S.; Jia, Z.; Lu, X.; Yu, H.; Chen, W.; Zhu, J.; Xie, R.; Shi, D.; Xu, X.; Xiang; J.; Liu, K.; Zhang, G. Observation of strong interlayer coupling in MoS₂/WS₂ heterostructures. Adv. Mater. 2016, 28, 1950–1956.

(16) Hill, H. M.; Rigosi, A. F.; Rim, K. T.; Flynn, G. W.; Heinz, T. F. Band alignment in MoS₂/WS₂ transition metal dichalcogenide heterostructures probed by scanning tunneling microscopy and spectroscopy. Nano Lett. 2016, 16, 4831–4837.

(17) Choudhary, N.; Park, J.; Hwang, J. Y.; Chung, H.-S.; Dumas, K. H.; Khondaker, S. I.; Choi, W.; Jung, Y. Centimeter scale patterned growth of vertically stacked few layer only 2D MoS₂/WS₂ van der Waals heterostructure. Sci. Rep. 2016, 6, 25456.

(18) Chhowalla, M.; Amaratunga, G. A. J. Thin films of fullerene-like MoS₂ nanoparticles with ultra-low friction and wear. Nature 2000, 407, 164–167.

(19) Winer, W. O. Molybdenum disulfide as a lubricant: a review of the fundamental knowledge. Wear 1967, 10, 422–452.
(20) Rapoport, L.; Fleischer, N.; Tenne, R. Applications of WS2(MoS2) inorganic nanotubes and fullerene-like nanoparticles for solid lubrication and for structural nanocomposites. J. Mater. Chem. 2005, 15, 1782–1788.

(21) Rapoport, L.; Leshchinsky, V.; Lapsker, I.; Volovik, Y.; Nepomnyaishch, O.; Lvovsky, M.; Popovitz-Biro, R.; Feldman, Y.; Tenne, R. Tribological properties of WS2 nanoparticles under mixed lubrication. Wear 2003, 255, 785–793.

(22) Rapoport, L.; Bilik, Y.; Feldman, Y.; Homyonof, M.; Cohen, S.; Tenne, R. Hollow nanoparticles of WS2 as potential solid-state lubricants. Nature 1997, 387, 791–793.

(23) Das, S.; Chen, H.-Y.; Penunamata, A. V.; Appenzeller, J. High performance multilayer MoS2 transistors with scandinium contacts. Nano Lett. 2013, 13, 100–105.

(24) Radisavljevic, B.; Whitwick, M. B.; Kis, A. Integrated circuits and logic operations based on single-layer MoS2. ACS Nano 2011, 5, 9934–9938.

(25) Ly, R.; Robinson, J. A.; Schaal, R. E.; Sun, D.; Sun, Y.; Mallouk, T. E.; Terrones, M. Transition metal dichalcogenides and beyond: synthesis, properties, and applications of single-and few-layer nanosheets. Acc. Chem. Res. 2015, 48, 56–64.

(26) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronic and optoelectronics of two-dimensional transition metal dichalcogenides. Nat. Nanotechnol. 2012, 7, 699.

(27) Ma, Y.; Dai, Y.; Guo, M.; Niu, C.; Lu, J.; Huang, B. Electronic and magnetic properties of perfect, vacancy-doped, and nonmetal adsorbed MoS2, MoTe2, and WS2 monolayers. Phys. Chem. Chem. Phys. 2011, 13, 15546–15553.

(28) Mak, K. F.; He, K.; Shan, J.; Heinz, T. F. Control of valley polarization in monolayer MoS2 by optical helicity. Nat. Nanotechnol. 2012, 7, 494–498.

(29) Dankert, A.; Langouche, L.; Kamalakar, M. V.; Dash, S. P. High-performance molybdenum disulfide field-effect transistors with spin tunnel contacts. ACS Nano 2014, 8, 476–482.

(30) Zhu, C.; Mu, X.; van Aken, P. A.; Yu, Y.; Maier, J. Single-layered ultrasmall nanoplates of MoS2 embedded in carbon nanofibers with excellent electrochemical performance for lithium and sodium storage. Angew. Chem. Int. Ed. 2014, 53, 2152–2156.

(31) Yu, X.-Y.; Hu, W.; Wang, Y.; Chen, H.; Lou, X. W. Layered ultrathin MoS2 Nanosheets Supported on N-doped Carbon Nanoboxes with Enhanced Lithium Storage and Electrochemical Properties. Angew. Chem. Int. Ed. 2015, 54, 7395–7398.

(32) Pumera, M.; Sofer, Z.; Ambrosi, A. Layered transition metal dichalcogenides for electrochemical energy generation and storage. J. Mater. Chem. A 2014, 2, 8981–8987.

(33) Shiva, K.; Matte, H. S. R.; Rajendra, H. B.; Bhattacharyya, A. J.; Rao, C. N. R. Employing synergistic interactions between few-layer WS2 and reduced graphene oxide to improve lithium storage, photocatalytic behavior of MoS2 and WS2 nanocluster sensitized TiO2. Langmuir 2014, 30, 566–575.

(34) Late, D. J.; Huang, Y.-K.; Liu, B.; Acharya, J.; Shirodkar, S. N.; Perkins, F. K.; Friedman, A. L.; Cobas, E.; Campbell, P. M.; Nørskov, J. K.; Cui, Y. Transition-metal doped edge sites in vertically aligned MoS2 catalysts for enhanced hydrogen evolution. Nano Res. 2015, 8, 566–575.

(35) Jernigan, G. G.; Jonker, B. T. Chemical vapor sensing with monolayer WS2 and reduced graphene oxide to improve lithium storage, photocatalytic behavior of MoS2 and WS2 nanocluster sensitized TiO2. Langmuir 2014, 30, 566–575.

(36) Wang, H.; Tsai, C.; Kong, D.; Chan, K.; Abild-Pedersen, F.; Narskov, J. K.; Cui, Y. Transition-metal doped edge sites in vertically aligned MoS2 catalysts for enhanced hydrogen evolution. Nano Res. 2015, 8, 566–575.

(37) Dai, X.; Du, K.; Li, Z.; Liu, M.; Ma, Y.; Sun, H.; Zhang, X.; Yang, Y. Co-doped MoS2 nanosheets with the dominant CoMoS phase coated on carbon as an excellent electrocatalyst for hydrogen evolution. ACS Appl. Mater. Interfaces 2015, 7, 27242–27253.

(38) Kong, D.; He, J.-H. Few-layer MoS2 with high broadband photogain and fast optical switching for use in harsh environments. ACS Nano 2013, 7, 3905–3911.

(39) Yang, J.; Majumdar, K.; Liu, H.; Du, Y.; Wu, H.; Hatzistergos, M.; Hung, P. Y.; Tiekkelman, R.; Tsai, W.; Hobbs, C.; Ye, P. D. Chloride molecular doping technique on 2D materials: WS2 and MoS2. Nano Lett. 2014, 14, 6275–6280.

(40) Ding, K.; Lin, Y.; Huang, M. The enhancement of NO detection by doping strategies on monolayer MoS2. Vacuum 2016, 130, 146–153.

(41) Wang, H.; Tsai, C.; Kong, D.; Chan, K.; Abild-Pedersen, F.; Narskov, J. K.; Cui, Y. Transition-metal doped edge sites in vertically aligned MoS2 catalysts for enhanced hydrogen evolution. Nano Res. 2015, 8, 566–575.

(42) Dai, X.; Du, K.; Li, Z.; Liu, M.; Ma, Y.; Sun, H.; Zhang, X.; Yang, Y. Co-doped MoS2 nanosheets with the dominant CoMoS phase coated on carbon as an excellent electrocatalyst for hydrogen evolution. ACS Appl. Mater. Interfaces 2015, 7, 27242–27253.

(43) Cheng, Y. C.; Zhu, Z. Y.; Mi, W. B.; Guo, Z. B.; Schwingenschloß, U. Prediction of two-dimensional diluted magnetic semiconductors: Doped monolayer MoS2 systems. Phys. Rev. B: Condens. Matter Mater. Phys. 2013, 87, 100401.

(44) Ramosubramaniam, A.; Navel, D. Mn-doped monolayer MoS2: an atomically thin dilute magnetic semiconductor. Phys. Rev. B: Condens. Matter Mater. Phys. 2013, 87, 195201.

(45) Lin, X.; Ni, J.; Charge and magnetic states of Mn, Fe-, and Co-doped monolayer MoS2. J. Appl. Phys. 2014, 116 (4), 043431. DOI: 10.1063/1.4891495

(46) Zhou, W.; Yin, Z.; Du, Y.; Huang, X.; Zeng, Z.; Fan, Z.; Liu, H.; Wang, J.; Zhang, H. Synthesis of few-layer MoS2 nanosheet-coated TiO2 nanobelt heterostructures for enhanced photocatalytic activities. Small 2013, 9, 140–147.

(47) Lee, G.-H.; Yu, Y.-J.; Cui, X.; Petrone, N.; Lee, C.-H.; Choi, M. S.; Lee, D.-Y.; Lee, C.; Yoo, W. J.; Watanebe, K.; Taniguchi, T.; Nuckolls, C.; Kim, P.; Hone, J. Flexible and transparent MoS2 field-effect transistors on hexagonal boron nitride-graphene heterostructures. ACS Nano 2013, 7, 7931–7936.

(48) Tessone, A. A.; Lewis, E. A.; Savjani, N.; Zhong, X. L.; Haigh, S. J.; O’Brien, P.; Lewis, D. J. Single-Source Precursor for Tungsten Dichalcogenide Thin Films: Mo1-xWxS2 (0 ≤ x ≤ 1) Alloys by Aerosol-Assisted Chemical Vapor Deposition. Chem. Mater. 2017, 29, 3858–3862.

(49) Lewis, D. J.; Tessone, A. A.; Zhong, X. L.; Lewis, E. A.; Rooney, A.; Savjani, N.; Brent, J. R.; Haigh, S. J.; Burke, M. G.; Murny, C. A.; Raftery, J. M.; Warrens, C.; West, K.; Gaemers, S.; O’Brien, P. Thin films of molybdenum disulfide doped with...
(99) Li, N.; Teng, H.; Zhang, L.; Zhou, J.; Liu, M. Synthesis of Mo-doped \( \text{WO}_3 \) nanosheets with enhanced visible-light-driven photocatalytic properties. RSC Adv. 2015, 5, 95394–95400.

(100) Guo, Y.; Quan, X.; Lu, N.; Zhao, H.; Chen, S. High photocatalytic capability of self-assembled nanoporous \( \text{WO}_3 \) with preferential orientation of (002) planes. Environ. Sci. Technol. 2007, 41, 4422–4427.

(101) Zhang, D.; Wang, S.; Zhu, J.; Li, H.; Lu, Y. \( \text{WO}_3 \) nanocrystals with tunable percentage of (0 0 1)-facet exposure. Appl. Catal., B 2012, 123–124, 398–404.

(102) Salje, E. Symmetry and lattice dynamics of oxides with perovskite-like structures. Acta Crystallogr., Sect. A: Cryst. Phys., Diff. Therm. Gen. Crystallogr. 1976, 32, 233–238.

(103) Mu, W.; Xie, X.; Li, X.; Zhang, R.; Yu, Q.; Lv, K.; Wei, H.; Jian, Y. Characterizations of Nb-doped \( \text{WO}_3 \) nanomaterials and their enhanced photocatalytic performance. RSC Adv. 2014, 4, 36064–36070.

(104) Morandi, S.; Paganini, M. C.; Giamello, E.; Bini, M.; Capsoni, D.; Massarotti, V.; Ghiotti, G. Structural and spectroscopic characterization of \( \text{Mo}_x \text{W}_{1-y} \text{O}_{3} \) mixed oxides. J. Solid State Chem. 2009, 182, 3342–3352.

(105) Boulova, M.; Lucazeau, G. Crystalline nanosize effect on the structural transitions of \( \text{WO}_3 \) studied by Raman spectroscopy. J. Solid State Chem. 2002, 167, 425–434.

(106) May, R. A.; Kondrachova, L.; Hahn, B. P.; Stevenson, K. J. Optical Constants of Electodeposited Mixed Molybdenum–Tungsten Oxide Films Determined by Variable-Angle Spectroscopic Ellipsometry. J. Phys. Chem. C 2007, 111, 18251–18257.

(107) Rao, C. N. R.; Gopalakrishnan, J.; VidyaSagar, K.; Ganguli, A. K.; Ramanan, A.; Ganapathi, L. Novel metal oxides prepared by ingenious synthetic routes. J. Mater. Res. 1986, 1, 280–294.

(108) Hibble, S. J.; Dickens, P. J. Hydrogen insertion compounds of the mixed molybdenum tungsten oxides \( \text{Mo}_x \text{W}_{1-y} \text{O}_{3} \) \((0 < y < 0.9)\) Mater. Res. Bull. 1985, 20, 343–349.

(109) Figlarz, M. New oxides in the \( \text{WO}_3 \)-\( \text{MoO}_3 \) system. Prog. Solid State Chem. 1989, 19 (1), 1–46.

(110) Lee, C.; Yan, H.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S. Anomalous lattice vibrations of single-and few-layer Mo\text{S}_2. ACS Nano 2010, 4, 2695–2700.

(111) Korn, T.; Heydrich, S.; Hirmer, M.; Schmutzler, J.; Schüller, C. Low-temperature photocarrier dynamics in monolayer Mo\text{S}_2. Appl. Phys. Lett. 2011, 99, 102109.

(112) Li, H.; Zhang, Q.; Yang, C. C.; Tsy, B. K.; Edwin, T. H. T.; Oliivre, A.; Baillargeat, D. From Bulk to Monolayer Mo\text{S}_2: Evolution of Raman Scattering. Adv. Funct. Mater. 2012, 22, 1385–1390.

(113) De Wolf, I. Micro-Raman spectroscopy to study local mechanical stress in silicon integrated circuits. Semicond. Sci. Technol. 1996, 11, 139–154.

(114) Berkdemir, A.; Gutiérrez, H. R.; Botello-Méndez, A. R.; Perea-López, N.; Elias, A. L.; Chia, C.-I.; Wang, B.; Crespi, V. H.; López-Urías, F.; Charlier, J.-C. Identification of individual and few layers of WS\text{2} using Raman Spectroscopy. Sci. Rep. 2013, 3, 1755.

(115) Zhao, W.; Ghorannevis, Z.; Amara, K. K.; Ping, J. R.; Toh, M.; Zhang, X.; Kloc, C.; Tan, P. H.; Eda, G. Lattice dynamics in monolayer and few-layer sheets of WS\text{2} and WS\text{e}2. Nanoscale 2013, 5, 9677–9683.

(116) Zhao, W.; Ghorannevis, Z.; Chu, L.; Toh, M.; Kloc, C.; Tan, P.-H.; Eda, G. Evolution of Electronic Structure in Atomically Thin Sheets of WS\text{2} and WS\text{e}2. ACS Nano 2013, 7, 791–797.

(117) Gutiérrez, H. R.; Perea-López, N.; Elias, A. L.; Berkdemir, A.; Wang, B.; Lv, R.; López-Urías, F.; Crespi, V. H.; Terrones, H.; Terrones, M. Extraordinary Room-Temperature Photoluminescence in Triangular WS\text{2} Monolayers. Nano Lett. 2013, 13, 3447–3454.

(118) Santato, C.; Oudziemkowski, M.; Ullmann, M.; Augustynski, J. Crystallographically oriented mesoporous \( \text{WO}_3 \) films: synthesis, characterization, and applications. J. Am. Chem. Soc. 2001, 123, 10639–10649.