

# Solution-Phase Synthesis of Vanadium Intercalated 1T'-WS<sub>2</sub> with Tunable Electronic Properties

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**ABSTRACT:** Metal ion intercalation into Group VI transition metal dichalcogenides enables control over their carrier transport properties. In this work, we demonstrate a low-temperature, solution-phase synthetic method to intercalate cationic vanadium complexes into bulk WS<sub>2</sub>. Vanadium intercalation expands the interlayer spacing from 6.2 Å to 14.2 Å and stabilizes the 1T' phase of WS<sub>2</sub>. Kelvin-probe force microscopy measurements indicate that vanadium binding in the van der Waals gap causes an increase in the Fermi level of 1T'-WS<sub>2</sub> by 80 meV due to hybridization of vanadium 3d orbitals with the conduction band of the TMD. As a result, the carrier type switches from p-type to n-type, and carrier mobility increases by an order of magnitude relative to the Li-intercalated precursor. Both the conductivity and thermal activation barrier for carrier transport are readily tuned by varying the concentration of VCl<sub>3</sub> during the cation-exchange reaction.

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**Keywords:** transition metal dichalcogenides, two-dimensional materials, intercalation, Hall effect, conductivity

Two-dimensional materials are attractive for nanoscale, flexible electronic devices, but greater control over their electronic properties—band gap, carrier mobility and density—is needed for more widespread application.<sup>1-7</sup> The highly anisotropic structure of transition metal dichalcogenides (TMDs) enables incorporation of guest atoms into the van der Waals gap without disrupting the chemical bonds in the two-dimensional layer. These intercalated atoms can have dramatic effects on the electronic properties of the TMD through electron transfer and orbital hybridization.<sup>8-16</sup>

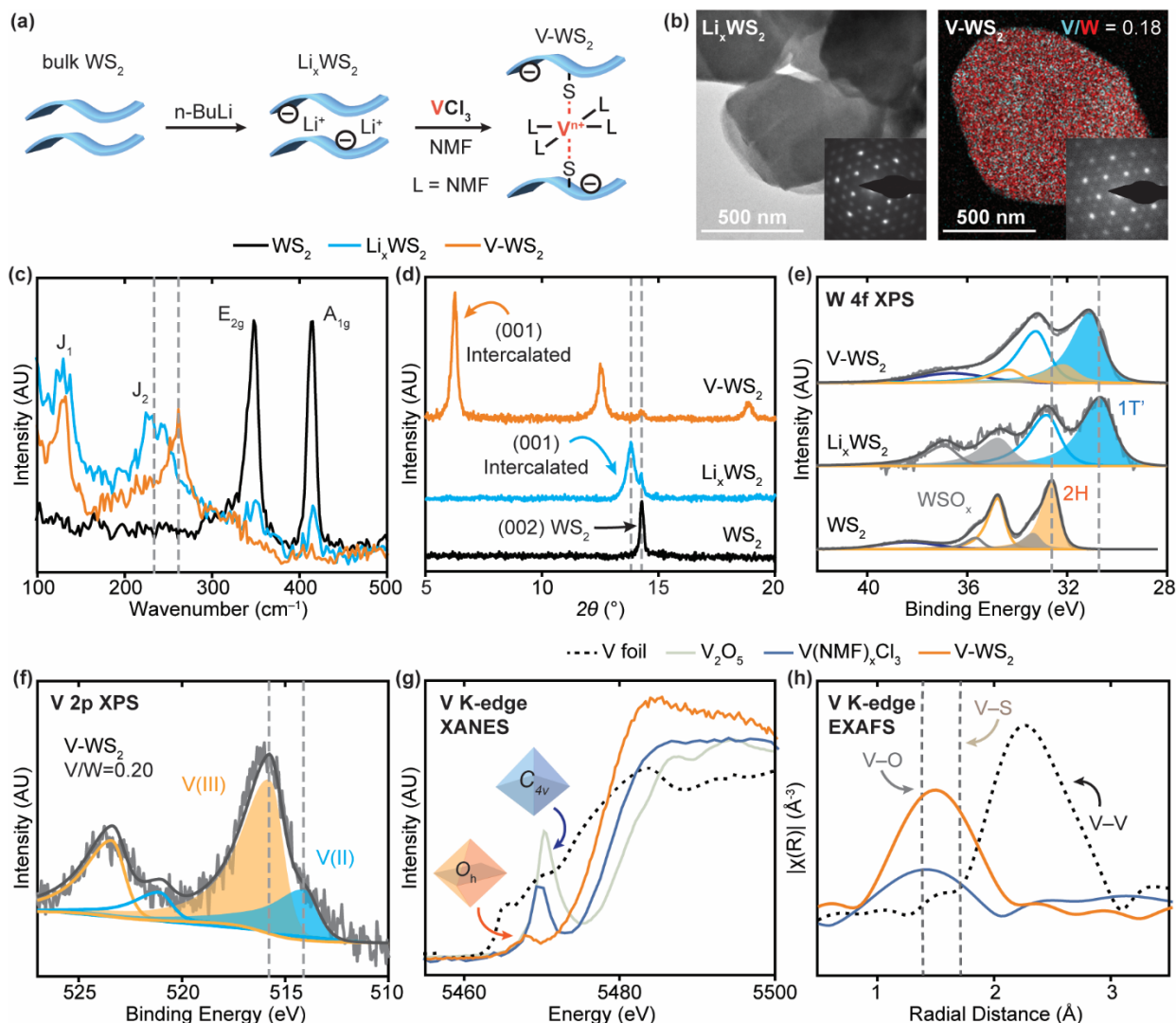
In most cases, the intercalation of a metal atom or cation is thermodynamically-driven by electron-transfer into the conduction band of the TMD, either from the intercalant atom itself or from an external reductant or reducing potential.<sup>17-25</sup> The majority of studies in the literature have focused on alkali ion intercalants because electron transfer is very favorable from the reducing alkali M<sup>0</sup> to the TMD.<sup>26-30</sup> Some non-alkali metal atoms can also be intercalated in this fashion, but the possible intercalant-TMD combinations as well as the extent of intercalation are limited by the relative energies of metal atom oxidation and the conduction band of the TMD.<sup>31-35</sup>

The charge-transfer intercalation strategy is particularly challenging for Group VI metal sulfides (MoS<sub>2</sub>, WS<sub>2</sub>) because of their high conduction band energies,<sup>36,37</sup> and only alkali metals have been capable of intercalating in high concentration.<sup>38-44</sup> To further functionalize the TMD, alkali-intercalated structures can undergo subsequent exchange with guest species through an exfoliation and restacking process.<sup>45</sup> While this method enables a wide diversity of intercalants—including cations,

organic molecules, inorganic complexes, and polymers—the exfoliation step in water significantly alters the morphological properties of the TMD and quenches the negative charge introduced by the alkali reductant.<sup>46-60</sup>

Electronically, alkali-intercalated MoS<sub>2</sub> and WS<sub>2</sub> have increased carrier densities and mobilities relative to the unintercalated TMD due to alkali electron transfer and conversion to the 1T' phase.<sup>26,61</sup> However, these structures are highly unstable to ambient atmosphere or protic solvent because the negative charge is entirely confined on the TMD.<sup>29,62,63</sup> In this work, we develop a solution-phase method to intercalate transition metal ions into bulk WS<sub>2</sub> through charge-transfer intercalation of Li followed by cation exchange to vanadium (**Figure 1a**). In doing so, we are able to stabilize the electronically-activated 1T' phase of WS<sub>2</sub> and further enhance carrier mobility through hybridization of the vanadium 3d orbitals into the conduction band. Synthesis of 1T-WS<sub>2</sub> substitutionally-doped with V atoms was also demonstrated recently using chemical vapor deposition.<sup>64</sup>

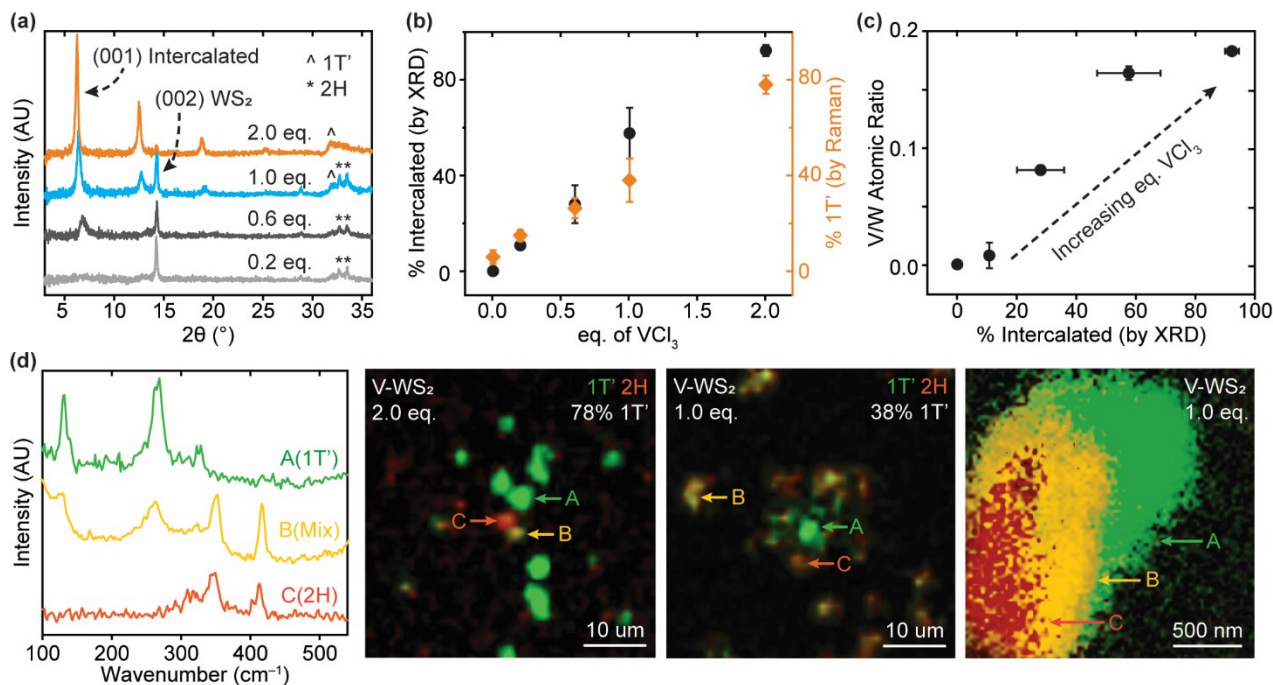
Bulk WS<sub>2</sub> is first reductively activated and intercalated with Li<sup>+</sup> using n-butyllithium (n-BuLi) based on literature methods.<sup>27</sup> Zeta-potential measurements of the lithiated WS<sub>2</sub> (Li<sub>x</sub>WS<sub>2</sub>) immediately after n-BuLi treatment reveals a strong anionic charge (−70 mV), which dissipates rapidly if exposed to O<sub>2</sub> and slowly if exposed to polar solvents under air-free conditions (**Figure S2**). To maximize the electrostatic interaction between the anionic TMD sheets and vanadium cations, we carry out the cation exchange reaction between Li<sub>x</sub>WS<sub>2</sub> powder and V<sup>3+</sup> precursors in N-methylformamide (NMF) solution for just 1 hour under N<sub>2</sub>.



**Figure 1.** (a) Schematic for the synthesis of intercalated V-WS<sub>2</sub>. (b) TEM image and SAED pattern of Li<sub>x</sub>WS<sub>2</sub> (left), EDS map and SAED pattern of V-WS<sub>2</sub> (right). (c) Raman spectra, (d) powder XRD patterns, and (e) W 4f XPS spectra of 2H-WS<sub>2</sub>, Li<sub>x</sub>WS<sub>2</sub>, and V-WS<sub>2</sub>. (f) V 2p XPS spectrum for V-WS<sub>2</sub>. (g) V K-edge XANES spectra and (h) V K-edge EXAFS spectra for V-WS<sub>2</sub> and control samples.

WS<sub>2</sub> undergoes significant structural changes during this two-step intercalation process. During n-BuLi activation, we observe a phase transition from the 2H phase to the distorted 1T' phase based on the  $2a \times 2a$  superlattice spots observed in the transmission electron microscope (TEM) selected-area electron diffraction (SAED) patterns (Figure 1b).<sup>40</sup> Raman spectra show the loss of the characteristic E<sub>2g</sub> and A<sub>1g</sub> vibrational modes of 2H-WS<sub>2</sub> and the appearance of the J<sub>1</sub> and J<sub>2</sub> modes of 1T'-WS<sub>2</sub> (Figure 1c).<sup>65-67</sup> Because the 1T' phase has a narrow bandgap (~110 meV),<sup>68,69</sup> diffuse-reflectance UV-Vis spectra show no absorption features (Figure S3). X-ray photoelectron spectra (XPS) of the W 4f peaks exhibit a characteristic shift to lower binding energy due to the phase transition (Figure 1e).<sup>70</sup> Powder X-ray diffraction (XRD) reveals an expansion of the interlayer galleries after lithiation. The (00n) peak shifts from 14.3° in bulk WS<sub>2</sub> to 13.9° in Li<sub>x</sub>WS<sub>2</sub>, an increase in interlayer spacing from 6.18 Å to 6.36 Å (Figure 1d). By comparing the relative areas of the two (00n) peaks, we estimate that 19% of the sample remains unintercalated due to the diffusional constraints of Li in large WS<sub>2</sub> microparticles.<sup>71</sup>

Upon reaction of Li<sub>x</sub>WS<sub>2</sub> with 2.0 equiv. VCl<sub>3</sub>, a further shift in the (00n) peak to 6.25° is observed, and the unintercalated WS<sub>2</sub> diffraction peak is suppressed (Figure 1d). The relative area of the two peaks indicates that 92% of the WS<sub>2</sub> material is intercalated with the large, solvated V<sup>n+</sup> complex. The observed interlayer distance of 14.2 Å is comparable to previous examples of hydrated Na<sup>+</sup> intercalated into MoS<sub>2</sub>.<sup>56</sup> A V:W atomic ratio of 0.18 is observed by energy-dispersive X-ray spectroscopy (EDS) and X-ray fluorescence (XRF) (Table S1), and V atoms are evenly distributed across the lateral surface of the WS<sub>2</sub> microparticle based on EDS mapping (Figure 1b, S4). Elemental analysis using XPS reveals a near-surface V:W ratio of 0.20 (Table S1), similar to the bulk ratio, which suggests that V species are also uniformly distributed throughout the thickness of the WS<sub>2</sub> sheet. XPS on the V 2p region shows that 30% of intercalants are partially reduced from V<sup>3+</sup> to V<sup>2+</sup> by the negatively charged Li<sub>x</sub>WS<sub>2</sub> sheets (Figure 1f). Correspondingly, a slight shift in the W 4f XPS peak to higher binding energy is observed due to consumption of excess electrons by V complexes (Figure 1e).<sup>25</sup>



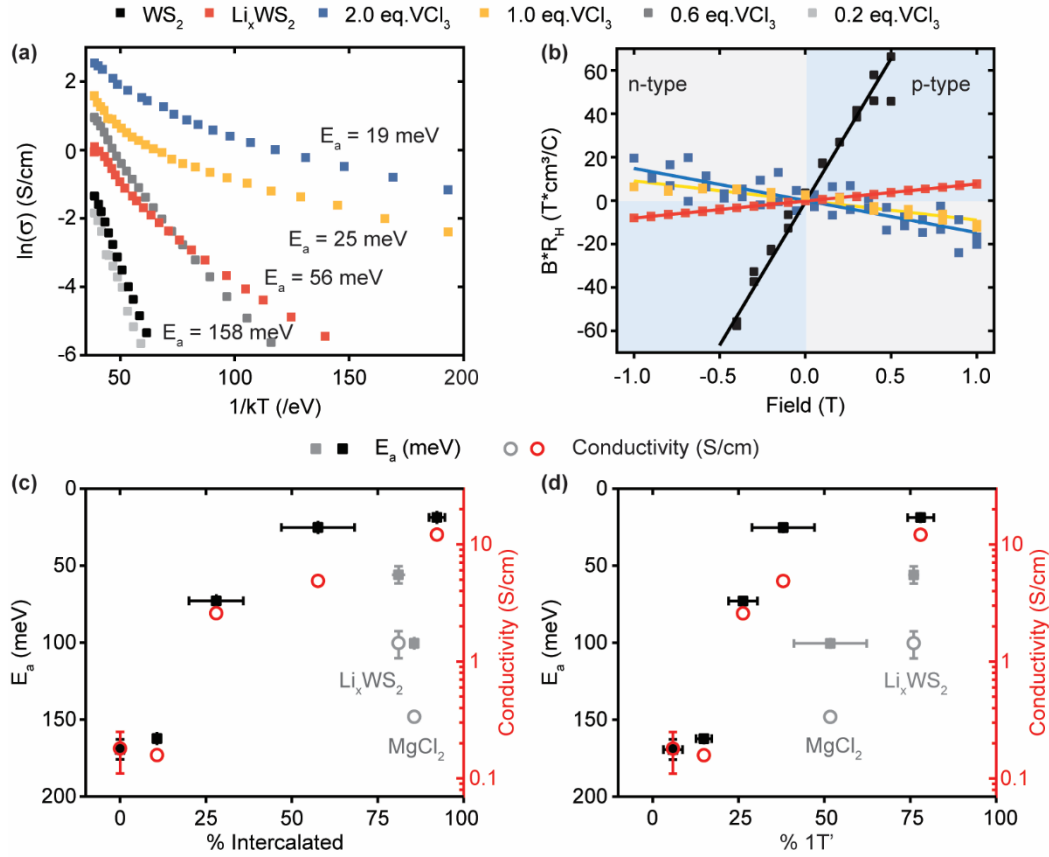
**Figure 2.** (a) Powder XRD patterns of V-WS<sub>2</sub> synthesized with varying equivalents of VCl<sub>3</sub>. (b) The percentage of the sample intercalated with V (left axis) and in the 1T' phase (right axis) as a function of VCl<sub>3</sub> equiv. (c) V/W atomic ratio vs. percentage of V-intercalated WS<sub>2</sub>. (d) Representative Raman spectra of 1T' (green), mixed phase (yellow), and 2H (red) regions and Raman maps of 2.0 and 1.0 equiv. V-WS<sub>2</sub>.

Raman spectra reveal an interesting change in the WS<sub>2</sub> interlayer coupling strength after V intercalation (Figure 1c). V-WS<sub>2</sub> remains predominantly in the distorted 1T' phase, but a significant blue-shift is observed in the J<sub>2</sub> mode, which represents a linear combination of the out-of-plane A<sub>1g</sub> mode and the longitudinal acoustic mode at the M point in the Brillouin zone.<sup>72-74</sup> The shift from 240 cm<sup>-1</sup> in Li<sub>2</sub>WS<sub>2</sub> to 260 cm<sup>-1</sup> in V-WS<sub>2</sub> indicates a strengthening of the interlayer coupling, likely because V<sup>2/3+</sup> ions can coordinatively bridge two WS<sub>2</sub> layers through the van der Waals gap.<sup>33</sup>

V K-edge X-ray absorption near edge spectroscopy (XANES) provides further information on the oxidation state and local coordination geometry of V atoms in V-WS<sub>2</sub> (Figure 1g). We compare the XANES spectrum to those of V metal foil, bulk V<sub>2</sub>O<sub>5</sub>, and the V precursor, prepared by dissolving anhydrous VCl<sub>3</sub> in NMF. The solvated precursor complex, V(NMF)<sub>6</sub>Cl<sub>3</sub>, has V K-edge energy of 5479.04 eV, which is characteristic of oxygen-coordinated V<sup>3+</sup> molecular complexes.<sup>75</sup> Upon intercalation into WS<sub>2</sub>, the V K-edge energy red-shifts by 1.69 eV, consistent with partial reduction to V<sup>2+</sup>. More interestingly, the intensity of the pre-edge feature at the V K-edge reports on the vanadium local coordination geometry.<sup>76</sup> Crystalline V<sub>2</sub>O<sub>5</sub> comprises only square pyramidal V<sup>5+</sup> ions and shows the highest intensity pre-edge feature at 5469.89 eV. The precursor V(NMF)<sub>6</sub>Cl<sub>3</sub> has an intermediate pre-edge intensity due to formation of a mixture of 4-6 coordinate complexes in solution. Critically, the V atoms in V-WS<sub>2</sub> show a weak pre-edge feature at 5465.77 eV, suggesting that the centrosymmetry of the V ion increases upon intercalation to adopt a pseudo-octahedral geometry through interaction with the WS<sub>2</sub> basal planes.

Further evidence of the change in V coordination is observed in the X-ray absorption fine structure (EXAFS) (Figure 1h). Both V-WS<sub>2</sub> and the V(NMF)<sub>6</sub>Cl<sub>3</sub> complex have their first coordination sphere scattering peaks at short radial distance, as expected for oxygen-based ligands bound to V<sup>2/3+</sup> (Table S2, Figure S5).<sup>77</sup> An increase in amplitude of the R-space peak for V-WS<sub>2</sub> compared to its precursor complex reflects an increase in coordination number. In addition, a slight shift to longer radial distance is observed. In literature vanadium structures, V-S bonds tend to be ~0.28 Å longer than V-O bonds (Table S3), and the small increase in average bond length for V-WS<sub>2</sub> may arise from the inclusion of S ligands in the first coordination sphere.

Varying the quantity of VCl<sub>3</sub> precursor in the cation-exchange step enables systematic variation of the intercalated V-WS<sub>2</sub> fraction. The XRD (001) peak position for the V-intercalated WS<sub>2</sub> remains at 6.25° regardless of the VCl<sub>3</sub> concentration, but the relative areas of the intercalated and non-intercalated (00n) peaks vary significantly (Figure 2a). The percentage of intercalated WS<sub>2</sub> drops from 92% at 2.0 equiv. VCl<sub>3</sub> to 58%, 28%, and 11% at 1.0, 0.6, and 0.2 equiv., respectively (Figure 2b). As controls, we stir the Li<sub>2</sub>WS<sub>2</sub> sample in pure NMF or MgCl<sub>2</sub>-containing solutions to understand the role of solvent and cation identity in the intercalation process. In NMF alone, Li<sup>+</sup> species diffuse out of the interlayer galleries, and no expanded d-spacing is observed in the XRD (Figure S6a). Mg<sup>2+</sup>, which has similar solvated ionic radius to V<sup>3+</sup>, shows full intercalation and similar interlayer spacing to the V-WS<sub>2</sub> samples (Figure S6b).



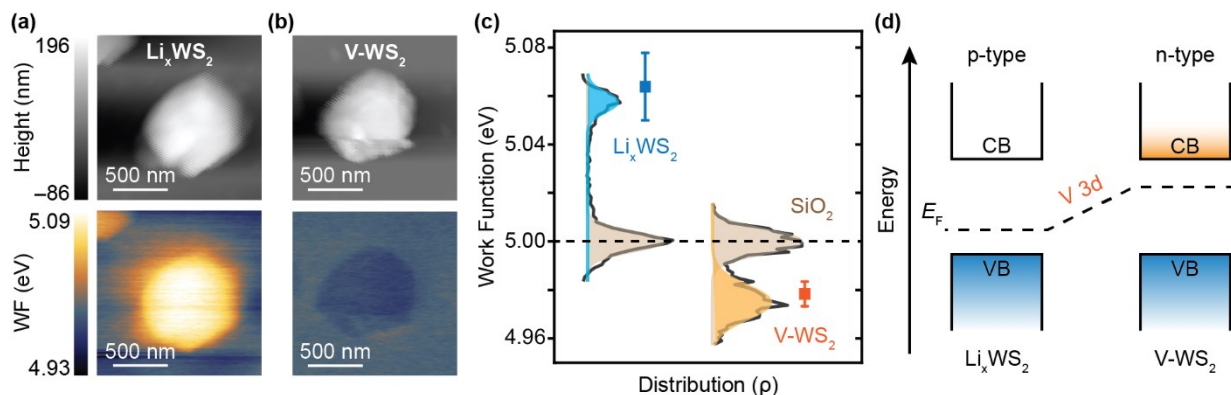
**Figure 3.** Electronic characterization of V- $\text{WS}_2$  and control samples. (a) Temperature-dependent conductivity plotted as  $\ln(\sigma)$  vs.  $1/kT$  and (b) Hall effect measurements. (c, d) Analysis of the carrier activation energy and room-temperature conductivity as a function of the (c) degree of intercalation and (d) 1T' phase retention.

During the cation-exchange reaction,  $\text{WS}_2$  sheets exhibit varying degrees of phase reversion from pure 1T' in  $\text{Li}_x\text{WS}_2$  to the 2H phase after stirring in NMF solution.<sup>28</sup> We utilize Raman mapping experiments to quantify the area percent of 1T' and 2H phases using the characteristic peaks at  $260 \text{ cm}^{-1}$  and  $414 \text{ cm}^{-1}$ , respectively (Figure 2d, S7). The 2.0 equiv. V- $\text{WS}_2$  sample shows the highest degree of 1T' phase retention (78%). The majority of  $\text{WS}_2$  microparticles remain in the 1T' phase (A) with a small number of particles exhibiting a mixture of phases (B) or the pure 2H phase (C). As the concentration of  $\text{VCl}_3$  precursor is reduced, a greater degree of phase reversion occurs (Figure 2b), but some phase-pure 2H and 1T' particles remain in every sample. Higher resolution mapping of mixed-phase particles in the 1.0 equiv. V- $\text{WS}_2$  sample shows an anisotropic distribution of phases even at the single sheet level (Figure 2d, S8a), and comparable spatial heterogeneity is observed for the V/W atomic ratio in EDS mapping (Figure S8b-c). These observations suggest that V intercalation is tied to phase stability and that a kinetic barrier exists for the phase reversion reaction, which depends on cation diffusion and microparticle edge structure. In the NMF-only control sample,  $\text{WS}_2$  converts entirely back to the 2H phase because there are no V ions in solution to replace the deintercalating  $\text{Li}^+$  (Figure S7, S9).  $\text{Mg}^{2+}$  shows an intermediate ability to stabilize the 1T' phase, retaining 51%.

Surprisingly, the quantity of V in the sample determined by XRF does not scale directly with the percentage of intercalated  $\text{WS}_2$ . (Figure 2c) The V/W ratio increases from 0.02 to 0.16 from 0.2 equiv. to 1.0 equiv.

$\text{VCl}_3$  but plateaus at that level from 1.0 equiv. to 2.0 equiv. despite the continued increase in intercalated  $\text{WS}_2$  percentage by XRD. The fraction of reduced  $\text{V}^{2+}$  species by XPS also remains relatively constant from 1.0 equiv. to 2.0 equiv. (Figure S10). The discrepancy between intercalated and total V suggests that intercalation occurs in a stepwise fashion, in which  $\text{V}^{3+}$  is first reduced and adsorbed at the edges of the  $\text{WS}_2$  microparticles followed by diffusion into the interlayer galleries, the latter of which becomes more favorable at higher concentrations of V precursor.

To understand the role of V intercalants on the electronic properties of  $\text{WS}_2$ , we conducted temperature-dependent conductivity and Hall effect measurements on pressed pellets in a 4-point van der Pauw configuration. While electronic transport measurements on pellets will necessarily be convoluted by grain boundaries, the presence of mixed phases, other structural heterogeneity, and the narrow band gap of the 1T' phase, comparisons between  $\text{Li}_x\text{WS}_2$  and V- $\text{WS}_2$  samples still provide useful structure-property correlations. Temperature-dependent conductivity measurements from 300 K to 60 K (Figure S12) illustrate that carrier transport is a thermally-activated process governed by the Arrhenius equation. Measurements on key samples were carried out in triplicate to insure the reproducibility of our synthetic method and pellet preparation (Table S4). Figure 3a shows Arrhenius plots for V-doped  $\text{WS}_2$  samples and undoped controls. We also obtained Hall effect measurements to determine the carrier type, density, and mobility for a subset of samples (Figure 3b, Table S5).



**Figure 4.** Kelvin-Probe Force Microscope (KPFM) measurements showing height and work function maps of (a)  $\text{Li}_x\text{WS}_2$  and (b)  $\text{V-WS}_2$ . (c) Histograms of the measured work function values extracted from the spatial map. (d) Band structure diagram illustrating the change in Fermi level with V intercalation.

Congruent with previous polycrystalline measurements in the literature (Table S6), the untreated 2H- $\text{WS}_2$  powder is a p-type semiconductor with carrier density of  $4.6 \times 10^{16} \text{ cm}^{-3}$ , and mobility of  $24 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The room temperature conductivity of the pellet is  $0.18 \text{ S cm}^{-1}$ , and the carrier transport activation energy is 158 meV. Upon lithiation, the conductivity increases to  $1.4 \text{ S cm}^{-1}$ , and  $E_a$  drops to 56 meV.  $\text{Li}$ -intercalated  $\text{WS}_2$  remains a p-type semiconductor, exhibiting an order of magnitude increase in carrier density ( $9.2 \times 10^{17} \text{ cm}^{-3}$ ) and a slight drop in carrier mobility ( $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) relative to the unlithiated sample. The electronic properties after lithiation stem from both the 2H to 1T' phase change as well as the injection of electrons from n-BuLi.<sup>26,78</sup> The much smaller bandgap of 1T'- $\text{WS}_2$  compared to 2H- $\text{WS}_2$  leads to the lower carrier activation energy and higher carrier density at 300 K.

The 2.0 equiv.  $\text{V-WS}_2$  sample, which has near complete formation of the intercalated structure and retention of the 1T' phase, shows another order of magnitude increase in room temperature conductivity up to  $12.1 \text{ S cm}^{-1}$  and decrease in  $E_a$  to 19 meV. Intriguingly, the dominant carrier type switches from p-type to n-type with carrier density of  $4.2 \times 10^{17} \text{ cm}^{-3}$ , and mobility of  $179 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . We hypothesize that hybridization of  $\text{V}^{2/3+}$  d-electrons with the conduction band of 1T'- $\text{WS}_2$  shifts the Fermi level towards the conduction band, thereby making electrons the dominant carrier and reducing the carrier transport activation barrier.<sup>79</sup> The V-intercalated  $\text{WS}_2$  samples prepared with lower equivalents of  $\text{VCl}_3$  exhibit electron transport properties commensurate with the amount of V intercalated into the  $\text{WS}_2$  sheets. Using 1 equiv.  $\text{VCl}_3$ , the carrier mobility and conductivity drop relative to the fully intercalated sample to  $58 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $6.5 \text{ S cm}^{-1}$ , respectively, while  $E_a$  and carrier density remain unchanged. Conductivity further decreases and  $E_a$  increases at 0.6 and 0.2 equiv. of  $\text{VCl}_3$ , falling near that of  $\text{Li}_x\text{WS}_2$  and 2H- $\text{WS}_2$ , respectively.

For the  $\text{Li}_x\text{WS}_2$  control stirred with NMF alone, the electronic and structural properties are similar to 2H- $\text{WS}_2$  (Figure S6). In general, samples that lack V intercalants and revert to the 2H phase exhibit low conductivity and high  $E_a$  values (Figure 3c-d). Increasing the concentration of  $\text{VCl}_3$  precursor increases both intercalation and 1T' percentage simultaneously, leading to improved electronic properties. Mg- $\text{WS}_2$  provides a useful control for a fully-intercalated sample containing a cation without d-orbitals capable of hybridizing with the  $\text{WS}_2$  conduction band. In this case, despite the 86% intercalation, the conductivity remains very low at  $0.33 \text{ S cm}^{-1}$ , in the same regime as the poorly intercalated V samples. Both the  $\text{Li}^+$  and  $\text{Mg}^{2+}$ -intercalated  $\text{WS}_2$  samples have lower conductivity and higher  $E_a$  relative to  $\text{V-WS}_2$  samples at similar levels of intercalation and 1T' phase retention, suggesting that 3d

electrons in the V-intercalants are crucial toward modulating the electronic properties of  $\text{WS}_2$ .

Pressed-pellet van der Pauw measurements provide the average electronic properties of the  $\text{V-WS}_2$  powder but may be convoluted by charge trapping and energetic barriers at grain boundaries.<sup>80</sup> To directly assess the electronic influence of V intercalants on the  $\text{WS}_2$  band structure, we performed single-particle Kelvin Probe Force Microscopy (KPFM) measurements on bulk  $\text{WS}_2$ ,  $\text{Li}_x\text{WS}_2$ , and 2.0 equiv.  $\text{V-WS}_2$  to determine the work function of each sample.<sup>81,82</sup> Samples were spun-coat onto a  $\text{SiO}_2$ -passivated Si wafer, and both the sample height and contact potential difference (CPD) between the tip and the surface were measured (Figure 4a-b, S13-14). Morphologically, all samples comprise micro-particles with lateral diameter of  $\sim 1 \mu\text{m}$  and thickness of 100–200 nm (Figure S15). To obtain the work function, we mapped 3 areas on each sample, each of which contained one  $\text{WS}_2$  particle surrounded by bare  $\text{SiO}_2$ . A CPD histogram was generated from each area, which was fit to two Gaussians to obtain the average CPD of the  $\text{SiO}_2$  substrate as well as the  $\text{WS}_2$  sheet (Figure 4c, S13-14). Because the absolute value of the CPD depends on the work function of the tip and varies across measurements, the  $\text{SiO}_2$  substrate is used as a reference with known work function of 5.00 eV to convert the CPD data into work function values.<sup>83,84</sup>

The results show that bulk  $\text{WS}_2$  has an average work function of 5.01 eV, similar to values reported in the literature.<sup>85</sup> Some spatial variation is observed moving from the edges to the center of the microsheet, which is consistent with a gradient in the spatial distribution of defects (Figure S13).<sup>86</sup> After n-BuLi treatment, the work function of  $\text{Li}_x\text{WS}_2$  increases to 5.06 eV, corresponding to a 50 meV drop in the Fermi level, because the distorted 1T' phase has a lower conduction band minimum and smaller band gap than the 2H phase (Figure 4a, c).<sup>85</sup> Vanadium intercalation results in a reduction in work function to 4.98 eV and correspondingly, an 80 meV increase in Fermi level compared to  $\text{Li}_x\text{WS}_2$  (Figure 4b, c). Given that  $\text{V-WS}_2$  and  $\text{Li}_x\text{WS}_2$  are both in the 1T' phase, we postulate that the interaction of V 3d electrons with the 1T'  $\text{WS}_2$  conduction band shifts the Fermi level toward the conduction band by 80 meV and leads to the observed change in carrier type from p-type to n-type (Figure 4d).

In conclusion, we have developed a solution-phase synthetic method to activate and intercalate  $\text{WS}_2$  with solvated V ions, which enables wide-ranging control over the carrier transport properties of V-intercalated 1T'- $\text{WS}_2$ . Detailed structural analysis using XRD and Raman spectroscopy shows that intercalation of V increases the interlayer spacing of  $\text{WS}_2$  by 8.02 Å while strengthening the interlayer coupling. Electronically, the carrier type switches from p-type to n-type, and the conductivity increases by an order of magnitude in  $\text{V-WS}_2$  compared to 1T'-

Li<sub>6</sub>WS<sub>2</sub>. Based on single-sheet KPFM measurements, these electronic changes stem from an increase in the Fermi level by 80 meV due to the interaction of V 3d orbitals with the WS<sub>2</sub> conduction band. This report provides the first example of charge-transfer intercalation of a solvated transition metal complex into the van der Waals gap of bulk WS<sub>2</sub>, showing a strong electronic hybridization despite its relatively disordered structure. This low-temperature, solution-phase synthetic strategy has the potential to expand the compositional diversity of transition-metal intercalated TMDs and enable facile control over their electronic properties.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Additional experimental details, materials, synthetic methods, physical characterization methods, electronic characterization methods, and supplementary figures and tables (PDF)

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### Notes

The authors declare no competing financial interests.

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