# Chemical scissor medicated intercalation of NbS<sub>2</sub> by transition metal for electromagnetic properties tuning

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# Abstract

Intercalation of layered materials offers an effective approach for tunning their structures and generating unprecedented properties. The multiple van der Waals (vdW) gap combined with long-range ordering guests can change the interaction of layered host materials and electromagnetic field. Herein, a chemical-scissor intercalation protocol medicated by molten salt is proposed for tailing the electromagnetic properties of transitional metal dichalcogenides (TMDCs). NbS<sub>2</sub> is functional

intercalated by heteroatoms (Fe, Co, Ni). The intercalated NbS<sub>2</sub> with superlattice exhibit improved the dielectric properties due to the reduced Brillouin zone size and the local electron distribution. Both the computational and experimental investigations indicate enhanced electron transport and additional polarized centers caused by intercalation. Overall, this work shows the great potential of structure editing of vdWmaterials, whilst intercalation *via* the chemical scissor in molten salts is considered a feasible intercalation strategy to further enrich their applications.

**Key words:** transition metal dichalcogenides, intercalation, superlattice, molten salts, dielectric modulation

## Introduction

Van der Waals (*vdW*) materials are often quasi-two-dimensional systems with strong in-plane bonding and the weak inter-layer coupling, and therefore sensitive to the changes in their surroundings environments. <sup>[1]</sup> Such materials including multilayer graphene, MXene, transitional metal dichalcogenides can provide the ideal interlayer space to accommodate guest species through intercalation. <sup>[2]</sup> Such a combination of two-dimensional (2D) layers and variable guests generates a flexible pathway to create a large family of functionalities for potential applications, such as energy storage, catalysis and electronic fields with desirable performances. <sup>[3]</sup> In addition, due to charge transfer within the layered host lattice, intercalation can profoundly alter chemical, electrical, optical, and magnetic properties of 2D materials.

It has been reported that the electronic structures of host materials can be tuned by flexible guest portfolios, <sup>[4]</sup> which can give rise to better electrical property simultaneously. <sup>[5]</sup> Notably, in artificial structures assembled from dissimilar *vdW* atomic layers, polarization and electron hopping are usually associated with different constituents. <sup>[6]</sup> Layered transition metal dichalcogenides (TMDCs), as typical *vdW* materials, have dielectric properties that are sensitive to both structural and electronic modulation. <sup>[7]</sup> The Group-V TMDCs, such as NbS<sub>2</sub>, are typically metallic material with good conductivity, promising applications in secondary batteries, catalysts and superconductors. <sup>[8]</sup> In this regard, the functional intercalation of TMDCs may hold a great promise for potential dielectric-related applications, such as electromagnetic wave (EMW) absorption material. <sup>[9]</sup> For example, the impedance unmatching of EMW materials tend to compromise their practical use. <sup>[10]</sup> Such an obstacle is known to have resulted from their non-ideal electronic property and structure limitations which may both be modulated by intercalation. <sup>[11]</sup>

Numerous reports for efficient EMW absorbers constructing strategy have previously emerged, such as core-shell <sup>[12]</sup>, flower-like <sup>[13]</sup>, urchin-like <sup>[14]</sup>, 3D framework <sup>[15]</sup>. Nonetheless, there are few reports on intercalated TMDCs in the field of EMW applications. The currently available intercalation methods for NbS<sub>2</sub> nanosheets are mainly based on chemical vapor deposition (CVD) at elevated temperatures <sup>[7d, 16]</sup>. While the preparation of *vdW* superlattices is difficult due to the limited yield and the damage to the material caused by each successive restacking or synthesis step <sup>[17]</sup>. The uncontrollable intercalation process and excessive crystallinity possess great challenges, especially on efficiently constructing intercalated TMDCs with atomic uniformity to achieve desired modulation of dielectric properties. Therefore, the lack of an effective intercalation method to ensure the strong binding state at superstructure interface may be the key barrier to hinder their application.

In this study, a versatile intercalation strategy with molten salt as solvent and metal powder as solvated guest is proposed. Metal atoms solvated in molten salt will generate a series of solvated electrons acting as gap-opening agents to assist the intercalation of metal atoms in to the host. <sup>[18]</sup> Such an approach provides a chemical-scissor way to functionalize TMDCs and ensures strong binding and uniform distribution. In this work, the chemical-scissor method is used as an alternative but effective approach to enhance the dielectric properties and application of TMDCs.

#### **Experimental and characterization**

*Synthesis of intercalated TMDCs:* Pristine NbS<sub>2</sub> was synthesized by solid-state reaction of elemental powders in a sealed quartz tube. Nb powder (300 mesh) and S

powder (200 mesh) with a molar ratio of 1:2.05 were thoroughly mixed in mortar and placed into quartz tube. The tube was evacuated by pump and then sealed with an  $H_2/O_2$  flame. The quartz tube was then placed in a muffle furnace and heated to 900 °C at a rate of 3°C per minute, where it was held for 10 hours. The muffle furnace was cooled down to the room temperature to yield the NbS<sub>2</sub> product.

Afterwards, LiCl-KCl molten salts were used as medicated protocol to assist intercalation. The pristine NbS<sub>2</sub> was mixed with the corresponding metal powders (200 mesh), respectively. Typically, the starting materials (including NbS<sub>2</sub>, Fe/Co/Ni powder and LiCl-KCl molten salt) were mixed thoroughly and placed into an alumina crucible. Detailed molar ratios of the materials are given in **Table S1**. These mixtures were then placed in an alumina crucible and heat-treated in a muffle furnace under Ar gas protection at 500 °C for 5 hours. After intercalation, the as-reacted products were washed by de-ionized water and ethanol, then dried at 40 °C for 2 hours.

*Characterization:* Crystal structure and composition of all samples were examined by Bruker D8 Advance X-ray diffractometer (XRD, with Ni-filtered Cu K $\alpha$  radiation, 40Kv, and 40 mA). The morphology was investigated by the thermal field emission scanning electron microscopy (SEM, Thermo scientific, Verios G4 UC). Atomic structures were examined in high-resolution transmission electron microscopy (HRTEM, Talos F200X) equipped with energy dispersive X-ray spectroscopy (EDX) system. The sample composition was identified by inductively coupled plasma optical emission spectroscopy (ICP–OES) on Agilent 700 Series spectrometer. Valence states were also collected in an XPS system (Thermo scientific escalab 250Xi) with a monochromatic Al K $\alpha$  X-ray source of X-ray photoelectron spectra (XPS). All binding energy (BE) peaks were calibrated by adjusting the C 1s peak at 284.8 eV.

*Computation Details*: All the calculations were performed by Vienna *Ab-initio* Simulation Package (VASP)<sup>[19]</sup>. The Perdew-Burke-Ernzerhof (PBE) functionals of generalized gradient approximation (GGA) were used to deal with the exchangecorrelation energy <sup>[20]</sup>. The projector augmented plane wave (PAW) method was adopted to deal with the interaction between nuclear electrons and valence electrons <sup>[21]</sup>. The GGA + U method was applied (U<sub>eff</sub> = 3 eV) to describe strongly correlated 3*d* electrons of the intercalated magnetic atoms. The cutoff energy was set to 520 eV and the Brillouin zone was sampled using  $9 \times 9 \times 3$   $\Gamma$ -center k-point grids. The criterion for energy and force convergences are  $1 \times 10^{-7}$  eV and 0.001 eV/Å, respectively. *Dielectric constant characterization:* The complex relative permittivity was measured by a Keysight E5063A ENA vector network analyzer. The complex permittivity ( $\varepsilon'$  and  $\varepsilon''$ ) and permeability ( $\mu'$  and  $\mu''$ ) of the pristine NbS<sub>2</sub> and M (M=Fe, Co, Ni)<sub>0.33</sub>NbS<sub>2</sub> were measured using the waveguide method with 40 wt% filler loading in wax. In addition, unintercalated molten salt treated blank NbS<sub>2</sub> was measured and the results are shown in the Supporting Information.



#### **Results and discussion**

Figure 1 (a) XRD patterns of pristine NbS<sub>2</sub> and intercalated M-NbS<sub>2</sub> (M= Fe, Co, Ni), insets show the (0003) peak of NbS<sub>2</sub> and intercalated-NbS<sub>2</sub>. (b) HRTEM images of Fe<sub>0.33</sub>NbS<sub>2</sub> along the [0001] zone axis. (c-d) SAED pattern of NbS<sub>2</sub> and Fe<sub>0.33</sub>NbS<sub>2</sub>. (e) HRTEM images of

 $Fe_{0.33}NbS_2$  along the  $[01\overline{1}0]$  zone axis. (f) Superlattice of intercalated  $Fe_{0.33}NbS_2$  along the [0001] zone axis. (g) Bright-field TEM image and EDS mappings of Nb, S and Fe in  $Fe_{0.33}NbS_2$ .

The intercalation behavior for M-NbS<sub>2</sub> (M= Fe, Co, Ni) are shown in **Figure 1**. In **Figure 1a**, XRD (0003) peaks of intercalated NbS<sub>2</sub> are observed shifting towards lower angles with phase distortion (from R3m to P6<sub>3</sub>2 $\overline{2}$ ), indicating that the expanded *c*-axis lattice and the similar structure after intercalation. <sup>[22]</sup> Such strong evidence for intercalation is related to both structural distortion and interaction between electrons. <sup>[23]</sup> On the one hand, the substantial strain energy induced by intercalated external species could be attributed to the expansion of the crystalline lattice. On the other hand, the lattice expansion could also be attributed to the self-motivated electron interaction between NbS<sub>2</sub> nanosheets and guest Fe/Co/Ni layer. Due to the dielectric difference, the electrons embedded in the *vdW* gap (valence electrons of Fe/Co/Ni) are inevitably transferred to the adjoining NbS<sub>2</sub> nanosheet with delocalized trend. <sup>[24]</sup> These delocalized electrons are then transferred to the not yet fully populated lowenergy dz<sup>2</sup> band of Nb <sup>[7d]</sup> (which is the lowest d-sub band in the wave manifold), thereby stabilizing the intercalated structure with the lowest energy.

The structure changes of Fe-NbS<sub>2</sub> after intercalation are identified along different zone-axis direction by the HRTEM image and SAED pattern. The local structure change in the a-b plane could be observed in **Figure 1b** along the [0001] zone-axis. The inset shows a hexagonal honeycomb area corresponding to the 2H-phase induced by intercalation. <sup>[25]</sup> . It is worth noting that 2H-phase NbS<sub>2</sub> possesses higher electron conductivity than 3R phase, as previously reported. <sup>[26]</sup> Further evidence of intercalation is provided by the selected area electron diffraction (SAED) along [0001] zone-axis direction in **Figure 1c-d. Figure 1c** shows one set of 6-fold symmetry diffraction spots, indicating the hexagonal phase of NbS<sub>2</sub>. Additionally, the commensurate superstructure reflection appears with a  $\sqrt{3}$ -fold periodicity (**Figure 1d**). As SAED results shown, the intercalated Fe-NbS<sub>2</sub> displays a  $\sqrt{3}a \times \sqrt{3}a$ 

superstructure in the a–b plane with a rotation of ~30°, which denotes two heterogeneous periodicities induced by additional guest. The corresponding superlattice is shown in **Figure 1e**. Furthermore, the interlayer distance along the  $[01\overline{10}]$  zone-axis (**Figure 1f**) expands from pristine 0.596 nm to 0.624 nm in Fe-NbS<sub>2</sub>, providing intuitive evidence of lattice expansion. The TEM image of the intercalated Fe-NbS<sub>2</sub> sample and its corresponding colored TEM energy-dispersive Xray spectrum (EDX) mapping of Fe is exhibited in **Figure 1g**. It has been found that the intercalated Fe is distributed throughout the host sheet and is further confirmed by the Fe peaks seen in the EDX spectra (**Figure S1**). The semi-quantitative Fe, Nb and S concentration in the nanosheets is about 10.9: 31.5: 57.6 at%. The lamellar integrity of NbS<sub>2</sub> maintained after intercalation, and the corresponding quantitative ICP data (**Table S2**) confirmed that the chemical formula of M (M=Fe, Co, Ni)-NbS<sub>2</sub> after intercalation is M<sub>0.33</sub>NbS<sub>2</sub>. Overall, the chemical scissor-medicated intercalation *via* molten salts provides a versatile protocol solution for editing the structure of TMDCs as well as introducing heterogeneous interfaces.

Worth notedly, the interlayer distance statistically indicated by XRD pattern in **Figure 1a** are not fully agreed with the ionic sizes of guest metals (Shannon's ionic radii:  $Fe^{2+}$ : 0.061 nm; Co<sup>2+</sup>: 0.065 nm; Ni<sup>2+</sup>: 0.069 nm). The discrepancy may be because the weak interlayer *vdW* interactions were replaced by Coulomb interactions after intercalation. The interlayer spacing is not only depends on structural distortion, but is also a function of the valence states, compound stability, and intrinsic electron redistribution. It has been reported that the electronic structures of host materials could be tuned controllably by intercalation treatment, <sup>[27]</sup> and the difference in the electronegativity of these atoms affects the overlap of the electron clouds.



Figure 2 Partial density of states (PDOS) of (a) pristine NbS<sub>2</sub> and intercalated (b) Fe<sub>0.33</sub>NbS<sub>2</sub>,
(c) Co<sub>0.33</sub>NbS<sub>2</sub>, (d) Ni<sub>0.33</sub>NbS<sub>2</sub>.

Therefore, we conducted first-principles spin-polarized calculations to obtain the electronic properties for the NbS<sub>2</sub> before and after intercalation. In order to understand the relationship between the electronic effect and the atomic-scale structure of  $M_{0.33}NbS_2$  (M=Fe, Co, Ni), we have performed density functional theory (DFT) calculations here. The results of calculation suggest that the guest M (M=Fe, Co, Ni) prefers to occupy the octahedral S-atom sites within the *vdW* gap, which is in line with our previous report <sup>[18b]</sup>. This preference could be attributed to the fact that the octahedral site provides a more favorable coordination environment and requires minimal structural reorganization to achieve stability. Additionally, an antiferromagnetic (AF) ordered state were identified further, which is consistent with previous reports. <sup>[16, 28]</sup> To gain further insight into the electron redistribution within intercalated NbS<sub>2</sub>, partial density of states (PDOS) and dipole moment of intercalated NbS<sub>2</sub> were investigated (**Figure 2**), with the Fermi level set to zero. Pristine NbS<sub>2</sub> exhibits typical metallicity due to a high density of electronic states near the Fermi

level (**Figure 2a**). This could be attributed to the half-filled *d* band of Nb. <sup>[16, 29]</sup> Notably, a profound modification of the band properties is evident in the PDOS calculations after intercalation (**Figure 2b-d**). Firstly, the Fermi level of intercalated NbS<sub>2</sub> shifts upwards to accommodate extra electrons transformed from guests (Fe, Co, Ni), resulting in a more filled  $d_z^2$  band. Subsequently, all electron density peaks have been weakened and flattened, accompanied by some degree of electron redistribution. The weakening of the S-*p* orbital can be attributed to the enhanced hybridization due to the transferred charge into the Nb conduction band, leading to non-equivalent Nb-S sites. The attractive potential of the adjacent positively guest ions (Fe, Co, Ni) ions will also expand the bonding state of the S-*p* electrons to some extent. As for Nb *d* band, the wider bandwidth is possibly a result of a mixture of conduction band electrons and charge accumulation from the accepted electrons. More importantly, the *d* orbital of intercalated guest (Fe, Co, Ni) indicates that guest orbitals significantly contribute to the PDOS near the Fermi level, leading to a broader bandwidth that may facilitate the electron hopping along *c*-axis. <sup>[30]</sup>



**Figure 3** (a) Side views of charge density difference of  $Fe_{0.33}NbS_2$  with [1010] viewing direction, yellow region: charge accumulation; blue region: charge depletion. (b-d) Nb 3*d*, S 2*p* and Fe 2*p* XPS analysis of intercalated Fe<sub>0.33</sub>NbS<sub>2</sub>

The charge density differences (CCD) of Fe<sub>0.33</sub>NbS<sub>2</sub> with [10 $\overline{1}0$ ] viewing direction, obtained by subtracting the total electron densities of NbS<sub>2</sub> and isolated guest (Fe, Co, Ni) atom in octahedral sites of the Fe<sub>0.33</sub>NbS<sub>2</sub> structure are presented in **Figure 3a**. The isovalue was set as 0.0075 eÅ<sup>-3</sup>, with charge depletion and accumulation in cyan and orange, respectively. A considerable alteration was observed in the charge accumulation region between Fe and S atoms. Bader charge analysis directly indicated charge flow amount, with a semi-quantitative electron transfer of 1.089 eV from Fe to Nb atoms. Furthermore, the inter-plane hybridization indicated by the dipole along *c*-axis after Fe intercalation, was calculated as 15.31 e·Å by DFT calculation, compared to the value of ~ 0 in pristine NbS<sub>2</sub>. That means, guests intercalated in the *vdW* gap could act as bridges for electronic transport between stacking layers, which might play a significant role in the dielectric response.

X-ray photoelectron spectroscopy (XPS) was further applied to investigate the chemical bonding environment of Fe<sub>0.33</sub>NbS<sub>2</sub>. Detailed information of pristine NbS<sub>2</sub> and full spectrum of the NbS<sub>2</sub> before and after intercalation could be found in **Figure S4-5**. The intercalated Fe 2*p* orbitals (**Figure 3b**) exhibit a pair of peaks located at 710.4 and 724.0 eV, corresponding to the  $2p_{3/2}$  and  $2p_{1/2}$  orbitals with Fe<sup>2+</sup> satellite peaks. The presence of low-valent Fe<sup>2+</sup> demonstrates the electron-donating role of Fe in intercalated NbS<sub>2</sub>, which further indicates a weak charge transfer process in the *vdW* interstitial site. As for Nb, before intercalation in pristine NbS<sub>2</sub> (**Figure S4**), the pair of splitting peaks could be attribute to Nb<sup>4+</sup> (3d<sub>5/2</sub>, 203.3 eV) and Nb<sup>4+</sup> (3d<sub>3/2</sub>, 206.4 eV) in the Nb-S bonding state. However, it is worth noting that the chemical environment of Nb changes fundamentally after intercalation. As shown in **Figure 3c**, two emerging pairs of Nb 3*d* orbital peaks, assigned to the reduced (Nb<sup>(4-x)+</sup>) and oxidized (Nb<sup>5+</sup>) bound states, newly appear at 202.6/205.5 eV and 206.7/209.2 eV, respectively. The occurrence appearance of lower valence Nb<sup>(4-x)+</sup> should be attributed to the partially filled 3*d* orbital accept the extra electrons from guest Fe. Moreover,

the appearance of  $Nb^{5+}$  should be attributed to the oxidation of intercalated  $NbS_2$  nanosheets.

As for the S 2*p* orbitals, the pristine NbS<sub>2</sub> showed a pair of doublet peaks at 160.4 and 161.9 eV, which could be assigned to the pristine Nb-S bond. However, the newly observed binding energy of S at 160.9 eV illustrates the bonding of Fe-S in intercalated  $Fe_{0.33}NbS_2$ . The emerging peak indicates that the original uniform sulfurbonded environment is disrupted and that Fe in the *vdW* gap induces the creation of new sulfur bound states. All the calculation analysis is consistent with the observed experimental results, demonstrating both the alteration of chemical environment and electron redistribution caused by electron transfer. Noted that these hybridized states around the Fermi level could contribute to improved conductivity. As a result, the intercalation medicated by chemical scissor in molten salts may readily induce substantial changes in the dielectric properties after intercalation.



**Figure 4** (a) Real part of permittivity, (b) imaginary part of permittivity, (c) tan  $\delta_{\varepsilon}$  of pristine NbS<sub>2</sub> and intercalated M (M=Fe, Co, Ni)<sub>0.33</sub>NbS<sub>2</sub> mixed with wax. (d) Conductivity calculated by utilizing the four-probe method. (e) Schematic illustration of the EMW absorption mechanism for intercalated NbS<sub>2</sub> *via* chemical scissor method

To gain an clearer insight into the significant effect of superstructure heterointerface on their device properties, the conductivity and electromagnetic wave (EMW) absorption performance of intercalated NbS<sub>2</sub> were investigated within a frequency range of 8.2–12.4 GHz (X band).The EMW absorption properties were found closely correlated with the complex permittivity ( $\varepsilon_r = \varepsilon' - j\varepsilon''$ ) and complex permeability ( $\mu_r = \mu' - j\mu''$ ) as shown in **Figure 4**. The real parts ( $\varepsilon'$ ) and imaginary parts ( $\varepsilon''$ ) of complex permittivity represent the storage and loss capacity for electric energy, while the real parts ( $\mu'$ ) and imaginary parts ( $\mu''$ ) of complex permeability represent the storage and loss capacity for magnetic energy. Noted that the  $\varepsilon'$  and  $\varepsilon''$ characterizes the polarization ability and dielectric loss caused by polarization relaxation, respectively.

The pristine NbS<sub>2</sub> exhibited a decrease in  $\varepsilon'$  value from 8.45 to 8.04, with a slight decrease in permittivity in accordance with Debye's law. After intercalation, these intercalated compounds exhibited a large degree of enhancement, with  $\varepsilon'$  varying from 14.3 to 12.9 for Fe<sub>0.33</sub>NbS<sub>2</sub>, 18.9 to 16.8 for Co<sub>0.33</sub>NbS<sub>2</sub>, 16.9 to 15.7 for Ni<sub>0.33</sub>NbS<sub>2</sub>, respectively. Similarly, compared with pristine NbS<sub>2</sub> ( $\varepsilon''$ : 1.3~1.1), an improved  $\varepsilon''$  were observed in Fe<sub>0.33</sub>NbS<sub>2</sub> ( $\varepsilon''$ : 6.2~4.2); Co<sub>0.33</sub>NbS<sub>2</sub> ( $\varepsilon''$ : 11.9~10.3) and Ni<sub>0.33</sub>NbS<sub>2</sub> ( $\varepsilon''$ : 7.4~6.7). Of note is that since the magnetic component showed very little change, all intercalated M<sub>0.33</sub>NbS<sub>2</sub> exhibit negligible magnetic storage and loss ability (**Figure S6**). This is consistent with the antiferromagnetic (AF) behavior obtained from DFT calculations in this and previous work <sup>[16, 28]</sup>. The AF state also suggests that there are few guest clusters in the intercalated NbS<sub>2</sub>, which further confirms that superstructure heterogeneous interfaces can be efficiently established by the chemical-scissor intercalation method.

Meanwhile, the changing trend of tan  $\delta_{\varepsilon}$  as shown in **Figure 4c**, is consistent with the evolving trends of  $\varepsilon''$ . Although there is no significant attenuation peak, the overall conductivity and dissipation increase due to the superlattice. This implies that the intercalated M<sub>0.33</sub>NbS<sub>2</sub> has stronger free electron hopping, which favors the formation of conductive networks and improves the conduction loss. This similar trend also indicates the electrical loss dominates the electromagnetic attenuation mechanism, further confirming the calculation results.

Moreover, a higher  $\varepsilon_r$  implies a higher conductivity based on the free electron theory <sup>[31]</sup>. The conduction loss could be attributed to the carrier migration and microcurrent, which is directly manifested in the electrical resistance and conductivity according to four-point probe method.

$$\sigma = \frac{1}{\rho} \tag{1}$$

Results show that the resistivity of pristine NbS<sub>2</sub>-wax (NbS<sub>2</sub>: wax= 40%: 60%) exceeds the test range (overscale than  $10^9$ ), so only the resistivity data of intercalated NbS<sub>2</sub> in the scale were presented in Figure S7. The conductivity exhibited in Figure 4d also follows the order of  $Co_{0.33}NbS_2 > Ni_{0.33}NbS_2 > Fe_{0.33}NbS_2$ . Such improved conductivity is negative correlation with the interlayer spacing (XRD peak position) shown in Figure 1a. Moreover, the interlayer spacing is correlated with the bonding iconicity between guest Fe/Co/Ni with surrounded S, which will greatly affect the electron interaction along the *c*-axis within the vdW gap <sup>[32]</sup>. Although the conductivity enhancement after intercalation has been confirmed by forementioned Fermi level calculation, it is not enough to demonstrate the order of conductivity. Therefore, to better understand the intrinsic conductive network arises from the charge transfer between the ordered metal guests and NbS<sub>2</sub> host, the electron work function (EWF) values of pristine NbS<sub>2</sub> and intercalated M<sub>0.33</sub>NbS<sub>2</sub> (M=Fe, Co, Ni) are calculated here. The EWF value for pristine NbS<sub>2</sub> is calculated as 5.80 eV. After intercalation, the EWF value for  $M_{0.33}NbS_2$  system (M=Fe, Co, Ni) decrease in the order of  $Co_{0.33}NbS_2$ , 1.02 eV <  $Ni_{0.33}NbS_2$ , 1.20 eV <  $Fe_{0.33}NbS_2$ , 1.41 eV. Usually, a lower value of EWF implies that electron transfer requires only a lower excitation energy to participate in the conductivity, <sup>[33]</sup> which is consistent with our experimental observation in Figure 4a-d. Overall, the elevated conductivity of the intercalated NbS<sub>2</sub> suggests that the improved electron migration and hopping, <sup>[34]</sup> which will improve the EMW performance by conduction loss<sup>[35]</sup>.

It is well known that dielectric loss originates from the conversion from EM wave energy to joule heat during the transmission of electric current within EM wave absorbers, which usually include conduction loss and polarization. <sup>[36]</sup> The dielectric loss enhancement mechanism of the intercalated NbS2 is shown in Figure 4e. Firstly, the long-ranger order of guests (Fe/Co/Ni) in the vdW gap has created new periodicity of superlattice as shown in Figure 1f. Moreover, such a longer-period superstructure in lattice space concerned a reduced-split Brillouin zone in reciprocal space, [37] while the resulting energy level splitting would not create new energy gaps. The conduction band after intercalation undergoes a greater energy expansion accompanied by the Bloch electrons in the superlattice. <sup>[38]</sup> These intercalated interfaces generate weakly localized states near the Fermi level, improving the electron mobility in both interplane and intraplane regions. Secondly, the electron redistribution interface could not satisfy the requirement of local charge neutrality, as charge carriers are fully depleted/accumulated, which leads to significant enhancement in electronic conductivity. Thirdly, multiple reflections and discontinuities in the current paths increase the transmission length of the electromagnetic wave and promote its scattering at multiple heterogeneous interfaces. Therefore, the localized current in the conductive network would be generated when incident EMW enters the intercalated NbS<sub>2</sub> superstructure, <sup>[39]</sup> enhancing the conduction loss of the incident EMW dissipation. In short, the guest (Fe, Co, Ni) embedded in the vdW gap form charge bridges that facilitate the electromagnetic waves interaction, which greatly promotes the electrical loss. <sup>[40]</sup>

As for the polarization, the induced long-range interactions tend to accumulate, forming a superposition polarization process with a wide range of relaxation times. The effect of polarization will be discussed in detail in the RL curve and Cole-Cole curve sections.



**Figure 5** Calculated reflection loss (RL) of pristine NbS<sub>2</sub>,  $Fe_{0.33}NbS_2$  and  $Ni_{0.33}NbS_2$  at the matching thickness ranging from 1.7 to 2.1 mm. b) 2D contour mappings of RL values at different thicknesses in the frequency range of 8.2–12.4 GHz.

In general, the EMW absorption performance of a material depends considerably on its electromagnetic parameters. To verify the feasibility of the chemical-scissor method in developing absorbers, reflection loss (RL, -dB), was used here as a key criterion to evaluate the EMW absorption performance of materials. Some new phenomena may emerge in terms of EMW absorption properties, which can be evaluated using RL curves and corresponding 2D contour mappings. RL could be calculated by transmission line theory, <sup>[41]</sup> which follows the formula (2):

$$RL(dB) = 20\log\left|\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right|$$
(2)

As is well known, the RL value of -10 dB equates to 90% EW absorption, and the corresponding bandwidth is denoted as the effective absorption bandwidth ( $E_{AB}$ ). A lower RL value and  $E_{AB}$ , along with a matching thickness indicates good performance. Typically, the  $E_{AB}$  of the absorbing material should exceed 2 GHz, with RL values below -10 dB at a thin matching thickness.

As shown in the RL versus frequency curves (Figure 5a), the bandwidth of  $\Delta f$ represents the total E<sub>AB</sub>, calculated by varying the coating thickness from 1.7 to 2.1 mm. In comparison to pristine NbS<sub>2</sub>, the intercalated NbS<sub>2</sub> exhibits varying degrees of improvement in E<sub>AB</sub>. Specifically, NbS<sub>2</sub>, Fe<sub>0.33</sub>NbS<sub>2</sub>, and Ni<sub>0.33</sub>NbS<sub>2</sub> covered  $\Delta f$  of 0, 4.2, and 4.2 GHz in the X band, respectively. The matching thickness was also reduced to 1.7 mm for Fe0.33NbS2 and EAB increased up to 3.45 GHz (8.91-12.36 GHz) for Fe<sub>0,33</sub>NbS<sub>2</sub>, which is higher than that obtained for pristine NbS<sub>2</sub> (0 GHz). The poor performance of pristine NbS<sub>2</sub> is attributed to its inability to form conductive networks and absence of interfacial polarization processes. It is worth noted that Co<sub>0.33</sub>NbS<sub>2</sub> and Ni<sub>0.33</sub>NbS<sub>2</sub> exhibit highest conductivity, while the desirable EMW absorption capacity observed is Fe<sub>0.33</sub>NbS<sub>2</sub>. More detailed RL data for pristine NbS<sub>2</sub> and intercalated NbS<sub>2</sub> at the matching thickness ranging from 1-3 mm could be found in Figure S8. In case of Co intercalated NbS<sub>2</sub>, the EMW absorption capacity still does not meet the criteria for dielectric absorbing materials, but for both Fe and Ni the absorption bandwidth has been significantly increase. Such inconsistence could be attributed to the over-enhanced conductivity, which tends to strengthen the reflection of electromagnetic waves and impede their effective dissipation within the material.

The corresponding 2D contour mapping of pristine NbS<sub>2</sub> and intercalated M<sub>0.33</sub>NbS<sub>2</sub> are shown in **Figure 5b-e**. Compared with the pristine NbS<sub>2</sub>, the intercalated NbS<sub>2</sub> shown variable degrees of improvement. The matching thickness is also reduced to 1.7 mm (**Figure 5c**) and 2.0 mm (**Figure 5e**) for Fe<sub>0.33</sub>NbS<sub>2</sub> and Ni<sub>0.33</sub>NbS<sub>2</sub>, respectively. The E<sub>AB</sub> increased up to 3.45 GHz (8.91-12.36 GHz) for Fe<sub>0.33</sub>NbS<sub>2</sub>, and 2.61 GHz (9.62-12.23 GHz) Ni<sub>0.33</sub>NbS<sub>2</sub>, which are higher than that obtained for pristine NbS<sub>2</sub>. The reduced matching thickness and wider effective bandwidth further improved the EMW absorption performance, which signify the feasibility of chemical-scissor intercalation approach to modulate the performance of EMW materials.

![](_page_16_Figure_0.jpeg)

**Figure 6** (a-c) Impedance match  $(Z_{in}/Z_0)$  curves 2D contour mappings of pristine NbS<sub>2</sub>; Fe<sub>0.33</sub>NbS<sub>2</sub>; and Co<sub>0.33</sub>NbS<sub>2</sub>. (d) The Cole-Cole plots of Fe<sub>0.33</sub>NbS<sub>2</sub>

Impedance mismatch is also a pressing issue for transition metal sulfide-based wave absorbers <sup>[9]</sup>. Therefore, impedance matching ( $Z_{in}/Z_0$ ) is another key factor to characterize excellent electromagnetic wave absorption performance, which must be considered when designing new and better microwave absorbers. As shown in **Figure 6**, the  $Z_{in}/Z_0$  value closer to 1.0 indicates a better impedance match, because EMW can only enter material interior if the material impedance is similar to the impedance of air. The corresponding formula (3) is illustrated as follows: <sup>[42]</sup>

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh\left[j\left(\frac{2\pi}{c}\right) f d\sqrt{\mu_r \varepsilon_r}\right]$$
(3)

In which  $Z_{in}$ ,  $Z_0$ , c, f and d are the impedance of air, the light velocity in a vacuum  $(3*10^8 \text{ m} \cdot \text{s}^{-1})$ , the incident waves frequency, and absorbers thickness, respectively.

It has been found that the impedance matching  $Z_{in}/Z_0$  of intercalated NbS<sub>2</sub> decreased significantly, compared with the high value of  $Z_{in}/Z_0 \sim 5$  (Figure 6a), the impedance for Fe<sub>0.33</sub>/Ni<sub>0.33</sub>NbS<sub>2</sub> are slightly less than 1 (see 3D  $Z_{in}/Z_0$  plots and 2D contour mappings of all samples in Figure S9-10), suggesting a lower matching thickness is desired for a better EMW absorption performance (RL<-10 dB) at X bands. While the poor EMW performance of Co<sub>0.33</sub>NbS<sub>2</sub> could be attributed to the small impedance mismatch value (<0.55) though it has the best conductivity.

In addition to conductivity, the contribution of polarization loss also matters to the EMW absorption performance, which usually is evaluated by the  $\varepsilon' - \varepsilon''$  curve. Theoretically, a long smooth line is associated with conduction losses, while a standard semicircle is referred as the perfect Debye relaxation. Such  $\varepsilon' - \varepsilon''$  plots denoted as the Cole–Cole semicircle deduced from Debye theory, <sup>[43]</sup> which can explain the attenuation behavior of these absorbers. As shown in **Figure S11**, the  $\varepsilon' - \varepsilon''$ plots of pristine NbS<sub>2</sub> exhibits typical conduction loss type with linear curves, suggesting a poor polarization. However, the intercalated Fe<sub>0.33</sub>NbS<sub>2</sub> manifests a strongly polarized behavior which is completely different to the one observed in pristine NbS<sub>2</sub> as shown in **Figure 6d**.

The ε'-ε" plots of Fe<sub>0.33</sub>NbS<sub>2</sub> present 3 distorted semicircles (marked with blue line), which indicate the existence of double medium relaxation process, each semicircle corresponding to a Debye dipole relaxation with additional polarization. <sup>[44]</sup> Firstly, the structural diploe originates from periodicity discontinuity and broken pristine symmetry. <sup>[45]</sup> The newly periodic arrangement of dielectric differences within the superlattices leads to collective interfacial dipole polarization. <sup>[46]</sup> Secondly, the appearance of polarized centers also originates from the chemically bound guest ions under EM fields. <sup>[36]</sup> Guests (Fe/Co/Ni) located in the octahedral interstices at the center of the S-octahedron can deviate from their intrinsic center position and vibrate within a certain range. The induced charge family mismatch (e.g., Nb<sup>4+</sup>/Nb<sup>(4-x)+</sup>,  $Fe^{x+}(NbS_2)^{x-}$ ) inevitably leads to polar at the interface <sup>[47]</sup>. Thus, the superstructure induced by intercalation has generated multiple polarized centers as shown in the charge density difference analysis (**Figure 3a**), which can improve the polarization strength of stacking 2D layer beside a-b plane. <sup>[48]</sup> Thirdly, although Fe<sub>0.33</sub>NbS<sub>2</sub> exhibit antiferromagnetic characteristic, some short-range charge ordering in the *vdW* gap could easily affect the dipole moment as indicated by DFT calculation. Then a network of dipole-dipole interaction along *c*-axis allows an eventual propagation of the polarization with a wide range of relaxation times, <sup>[49]</sup> as suggested by the distortion Cole-Cole semicircle. Overall, inevitable charges flow is induced in a well-intercalated heterogeneous structure, which tends to form multiple hole/electrons at heterogeneous interfaces, generating inter-dipole vibrations to enhance dielectric properties.

# Conclusion

A chemical-scissor intercalation strategy was proposed in this work to achieve intercalation in TMDCs, resulting in superlattice interfaces with local electron distribution in reduced Brillouin zone. The intercalated NbS<sub>2</sub> exhibit good synergistic effect in enhancing dielectric properties, including superlattice conductive networks and interface polarization propagation. The accumulated electrons and heterointerfaces within the guest-host Fe<sub>0.33</sub>NbS<sub>2</sub> superstructure significantly impacts dielectric effects, as jointly revealed by transmission electron microscopy and density functional theory calculations. As a result, the intercalated NbS<sub>2</sub> superstructure possess enhanced electrical loss and superior broader-frequency absorption covering the X band. These findings underscore the significance of intercalation by chemical scissor strategy, which is expected to pave new avenues for engineering 2D nanomaterials with tunable dielectric properties.

#### Supplemental information

Supporting Information is available from the Wiley Online Library or from the author.

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### **Declaration of interests**

The authors declare no competing interests.

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