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3d Transition Metal Coordination on Monolayer MoS₂: A facile doping method to functionalize surfaces

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Abstract

Two-dimensional materials (2DM) have attracted much interest due to their distinct optical, electronic, and catalytic properties. These properties can be tuned by a range of methods including substitutional doping and, as recently demonstrated, by surface functionalization with single atoms, thus increasing the 2DM portfolio. We theoretically and experimentally describe the coordination reaction between MoS₂ monolayers with 3d transition metals (TMs), exploring their nature and MoS₂-TMs interactions. Density Functional Theory calculations, X-Ray Photoelectron Spectroscopy (XPS), and Photoluminescence (PL) spectroscopy point to the formation of MoS₂-TM coordination complexes, where the adsorption energy for 3d TM resembles the crystal-field (CF) stabilization

energy for weak-field complexes. Pearson's theory for hard-soft acid-base and Ligand-field theory were used to discuss the periodic trends on 3d TM coordination on MoS₂ monolayer surfaces. We found that softer acids with higher ligand field stabilization energy, such as Ni²⁺, tend to form bonds with more covalent character with MoS₂, which can be considered a soft base. On the other hand, harder acids, such as Cr³⁺, tend to form more ionic bonds. Additionally, we studied the trends in charge transfer and doping observed by XPS and PL results, where metals like Ni led to n-type doping. In contrast Cu functionalization results in p-type doping. Therefore, the formation of coordination complexes on TMD's surface is a potentially effective way to control and understand the nature of single-atom functionalization of TMD monolayers without rely or create new defects.

Keywords: 2d materials, coordination chemistry, single-atom, surface functionalization

Introduction

In 2D materials (2DM), functionalization and doping are commonly accomplished through the induction of vacancies within the crystalline lattice or through the formation of substitutional sites, where atoms with a greater or lesser number of electrons are placed as dopants for the creation of semiconductors of type n or p, or through the formation of covalent bonds between organic molecules and atoms at the edges of the materials.¹⁻⁴ However, these interactions can be unstable and/or significantly alter the crystalline structure of 2D materials, thus modifying their intrinsic properties and stability. It was recently proposed that the physical adsorption of organic molecules or metallic atoms as a functionalization method can be an effective and damage-free way of altering the properties of 2D materials.⁵⁻⁷

Lei *et al.* showed theoretically and experimentally that the presence of nonbonding electron pairs on the surface of InSe could be exploited by applying Lewis acid-base concepts.⁸ Thus, simple acid-base reactions could be explored to form complexes between Lewis acids, such as Ti⁴⁺, and 2D materials. Depending on the strength of the acid, it is possible to control the material's Fermi level and bandgap.⁸ This opens a vast range of potential applications for these materials to fabricate photovoltaic devices. In this context, Ding *et al.* showed by Density Functional Theory (DFT) that the adsorption of 3d transition metal (TM) atoms on phosphorene surface is favorable, except for Zn.⁹ Similarly, Arqum *et al.* showed by DFT that transition metals coordinate at a "triangular"

site on the surface of phosphorene, and the geometry resembles that of an octahedral coordination complex.¹⁰ This concept can be expanded to other 2D materials, such as graphene and transition metal dichalcogenides (TMDs).¹¹

Recently Gangwar *et al.* studied via DFT the interactions of first row Single Atom of Transition Metal (SA-TM) with MoS₂.¹² They found that hollow sites (i.e., the position at the center of the hexagons) and Mo sites had very close adsorption energies, both being higher than for S sites. The trend observed follows the energy stabilization profile of crystal field (CF) for high-spin complexes, which should explain why the interaction with Zn is not favorable. These authors predicted that there is some coexistence of ionic and covalent bonding between the TM and MoS₂.¹² In this context, Hai *et al.* described theoretically and experimentally how the TM functionalization of MoS₂ could affect oxygen evolution reactions (OER) on its surface. The MoS₂-TM complexes were synthesized by hydrothermal treatment, and the results showed a monoatomic dispersion functionalization. They found a relationship between TM-S and TM-O bond order with the OER activity.¹³ Liu *et al.* developed a MoS₂-Co catalyst for hydrodeoxygenation. The catalyst was made by hydrothermal treatment, and the Co atoms were dispersed atomically and occupied the Mo, hollow, and S vacancy sites randomly.¹⁴

Although all these works successfully described the formation of MoS₂-TM complexes, the fundamentals of SA-TM TMDs doping and the effects of the TM coordination sphere on the doping level are still missing. Furthermore, a more controllable functionalization with TM is still needed.¹⁵ We recently showed that isolated Au atoms on the MoS₂ surface cause electrons to flow out of the 2D material, increasing the hole concentration on MoS₂.¹⁶ DFT theoretical results revealed that changes in the TM coordination sphere could adjust the MoS₂-TM binding energy. For example, the energy of the MoS₂-Au bond is twice as high when one coordination site on the Au atom is filled by one S atom on the surface of MoS₂ and the other three by Cl anions than when no Cl is present. When Cl anions are present, the electron transfer from MoS₂ to Au is more efficient, leading to more effective p-type doping and better performance in field-effect transistors. Additionally, the electronic band dispersion of MoS₂-Au is drastically affected by the number of Cl atoms on the Au coordination sphere.¹⁶

Here, we expanded this vision to evaluate the functionalization of MoS₂ monolayer with several 3d transition metal ions (Cr, Mn, Co, Ni, Cu, and Zn). We focus on the MoS₂-TM interaction to evaluate the formation of coordination complexes on the surface and correlate their properties with classical coordination complexes, thus facilitating functionalization and controlling its optical and chemical properties with minimal damage to the

crystalline monolayer. First, the coordination of 3d TM was evaluated by DFT, considering the interaction between MoS₂ and single TM or TM-Cl₃ species. The theoretical calculations were confirmed by X-Ray photoelectron spectroscopy (XPS), photoluminescence (PL) spectroscopy, and reflection electron energy loss spectroscopy (REELS). Additionally, the samples were characterized by optical, atomic force, scanning electron, and high-resolution transmission electron microscopy, which confirmed the monolayer nature of MoS₂ and the single atom nature of the functionalization with metals such as Ni. Finally, all observed trends are rationalized in terms of crystal-field stabilization energy, the absolute hardness of the 3d TM, and their reduction standard potentials with respect to the MoS₂ conduction and valence bands.

Methods

The synthesis of monolayer MoS₂ was carried out by a salt-assisted CVD method. A detailed description can be found in our previous publication.¹⁶ The flakes were transferred to a pristine Si/SiO₂ substrate to remove the excess Na salt and MoO₃ used in the growth process.

Functionalization of MoS₂. The MoS₂-TM complex formation was performed by dipping the Si/SiO₂ substrate with the CVD MoS₂ into an ethanol solution of chromium acetate (Cr₂(CH₃COO)₄(H₂O)₂), manganese acetate (Mn(CH₃COO)₂), iron (III) chloride (FeCl₃), cobalt chloride (CoCl₂), nickel chloride (NiCl₂), copper sulfate (CuSO₄), or zinc chloride (ZnCl₂) with concentrations between 1×10⁻³ and 1×10⁻⁹ mol L⁻¹ for 10 min. The functionalized MoS₂-TM sample was then immersed in isopropanol (IPA) for a few seconds to remove excess of transition metal salts, followed by N₂ drying. Finally, the sample was kept in vacuum for 10 min before the measurements. Pristine samples were also washed with ethanol and IPA, dried with N₂, and kept in vacuum for 10 minutes to exclude the effect of ethanol or IPA adsorption on the flake surface.

Raman and photoluminescence (PL) spectroscopy were performed by excitation at 488 nm in a Microscope-based Renishaw INVia Spectrometer with thermoelectric CCD. For samples of each different transition metal concentration, we characterized approximately the same region of the same flake before and after functionalization. At least five different flakes were measured for each MoS₂-TM complex and TM concentration. PL mappings

were obtained using an Alpha 300R Witec confocal Raman microscope with a highly sensitive EMS detector at 488 nm excitation wavelength and 2mW laser power.

XPS and REELS measurements were conducted in a high-resolution Thermo Scientific ESCALAB 250Xi spectrometer equipped with an electron energy hemispherical analyzer and using monochromatized Al K α line (1486.6 eV) excitation. The spectra were energy referenced to the C1s signal of aliphatic C atoms at the binding energy of 284.8 eV. XPS spectra were collected using X-ray beam spot size = 650 μ m with an emission angle of 90° with respect to the sample surface. High-resolution spectra were acquired with 25 eV pass energy. REELS spectra were acquired with the electron source operating at 1 keV.

The computational approach to study the equilibrium structure, stability, and electronic structure of transition metal-doped MoS₂ is based on the SIESTA package's DFT. We used DZP localized basis, norm-conserved pseudopotentials with Troullier-Martins parametrization, mesh cutoff energy of 350 Ry, and k points sampling of Brillouin zone in Monkhorst-Pack algorithm with 10 x 10 x 1 grid. The exchange-correlation functional used is based on PBE generalized-gradient approximation. The calculations were performed within a supercell framework with 3 x 3 unit cells and considering a 8.3% degree of functionalization. All calculations were done considering T = 0K, and the Fermi level was determined by the average energy of the highest occupied level at the valence band and the lowest unoccupied level. The optimized structure was used for the STEM image simulation using the Prismatic Software..¹⁷ Simulation parameters such as acceleration voltage, spherical aberration (C₃ and C₅), convergence angle, and inner/outer angle for the HAADF detector were set according to experimental conditions.

Microscopy imaging. Aberration corrected High-Resolution Scanning transmission electron microscopy (AC-HRSTEM) was carried out in an FEI Titan³ G2 60/300 operated at 80 kV to reduce irradiation damage. A high-angle annular dark-field (HAADF) detector collected the annular dark-field (ADF) signal. A Gaussian blur filter was applied using the *ImageJ* software to reduce the noise and enhance the visibility of the detailed structure. Raw images were used for acquiring the line profile of the ADF intensity. It is worth noting that prior to the STEM imaging, the CVD-grown MoS₂ was transferred to a TEM grid and then functionalized by 1 \times 10⁻⁶ mol L⁻¹ TM precursor in ethanol solution. Scanning electron microscopy (SEM) was carried out in a PhenomProX

(ThermoFisher, Waltham, EUA), operated at 15 kV with a backscattered electron detector. Atomic force microscopy (AFM) images were recorded on a Bruker ICON system in tapping mode using a RTESPA-300 tip.

Results

Prediction of MoS₂-TM complexes via DFT

First, a screening simulation was carried out to evaluate the general trend of the coordination of different transition metals on the MoS₂ surface and correlate these trends with the classical coordination chemistry theory to rationalize the properties of chemically functionalized MoS₂-TM complexes. Figures 1a, b, and c show the optimized structures for the semiconductor 1H phase of MoS₂ and the coordination of Co on two different coordination sites on the MoS₂ monolayer. There are three available coordination sites, which we name the H, M, and S sites (Figure 1a). In the M site, the coordinated metal is located on top of one Mo atom and bound to 3 S atoms, as shown in Figure 1b. In site H, the TM is located over the center of the MoS₂ hexagonal structure and bound to 3 S atoms, as shown in Figure 1c. When the metal is coordinated with the S site, it is located directly on top of one sulfur atom and bound just to that atom, as the Au atoms reported in a previous work from our group.¹⁶ As discussed in that work,¹⁶ the TM coordination sphere significantly impacts their properties when bound to the MoS₂ surface. Thus, we considered two different cases in all calculations. In the first one, the TM is bound to the MoS₂ as a single adatom, named here MoS₂-TM. For the other case, the TM's coordination sphere was completed by Cl atoms forming an octahedral structure around the TM, where it is bound to three S and three Cl atoms, labeled MoS₂-TM-Cl₃.

Figure 1d shows the adsorption energy, E_{ads} , modulus as a function of the number of electrons in the 3d orbitals. E_{ads} is defined as: $E_{\text{ads}} = E_{\text{MoS}_2\text{-TM}} - (E_{\text{TM}} + E_{\text{MoS}_2})$, where $E_{\text{MoS}_2\text{-TM}}$ is the energy of the final MoS₂-TM complex, and $E_{\text{TM}} + E_{\text{MoS}_2}$ is the sum of the energies of the isolated TM and MoS₂, respectively (Table S1). A clear trend resembles the one observed for the crystal field stabilization energy and the hydration enthalpy for weak field 3d TM complexes^{18,19}. The closed shell (d¹⁰) and the half shell (d⁵) cases exhibit the lowest adsorption energies due to the spherical symmetry of this electronic configuration. For other configurations, the non-symmetrical electronic distribution and the degeneracy loss of 3d orbitals lead to a stability gain upon the coordination, increasing the adsorption energy, as one can see for Ni with a d⁸ electronic configuration. These results are in agreement with the

ones reported by Karthikeyan et al. using a different DFT approach based on VASP code with the PBE exchange and correlation function.²⁰

To determine the most stable coordination site, we plotted the adsorption energy difference between the H and M sites for all 3d TMs, as shown in Figure 1e. Here, negative values indicate that the M site is the most stable, and positive values mean that the H is the most favorable coordination site. As one can see, the H site is the most favorable coordination site for MoS₂-TM, except for Sc and Cu that adsorb at the M sites. In addition, for all the MoS₂-TM-Cl₃ complexes, there are only slight energy differences between the H and M sites, with the M site showing slightly higher E_{ads} for all TMs, except for the Sc and Cu. This trend indicates that for all MoS₂-TM-Cl₃ complexes, there are no preferable adsorption sites. For all 3d TMs, the S site was not stable, and the H or M sites showed the highest values of E_{ads}.

Figure 1f shows the TM's partial charge for MoS₂-TM and MoS₂-TM-Cl₃ complexes analyzed by the Voronoi deformation density method²¹. We notice that TMs with a harder acid character (Sc, Ti, and V) tend to donate more electrons and stabilize with higher positive charge, meaning that the metal-sulfur interaction exhibits some ionic nature. This behavior is related to these metals' small ionization energy, leading to a greater tendency to lose the 4s and 3d electrons, leaving the atom with a closed shell and exhibiting higher positive charges. In contrast, for softer metals, such as Co, Ni, and Cu, there is a tendency to form stronger covalent bonds, increase the charge delocalization, and decrease the metal's charge. Since sulfur atoms have a soft base character, the interaction with soft metals has a higher adsorption energy due to its more covalent character, as seen by the high E_{ads} for Co and Ni. Furthermore, when the TM's coordination sphere is completed with Cl atoms, the partial charge is higher for all 3d metals.

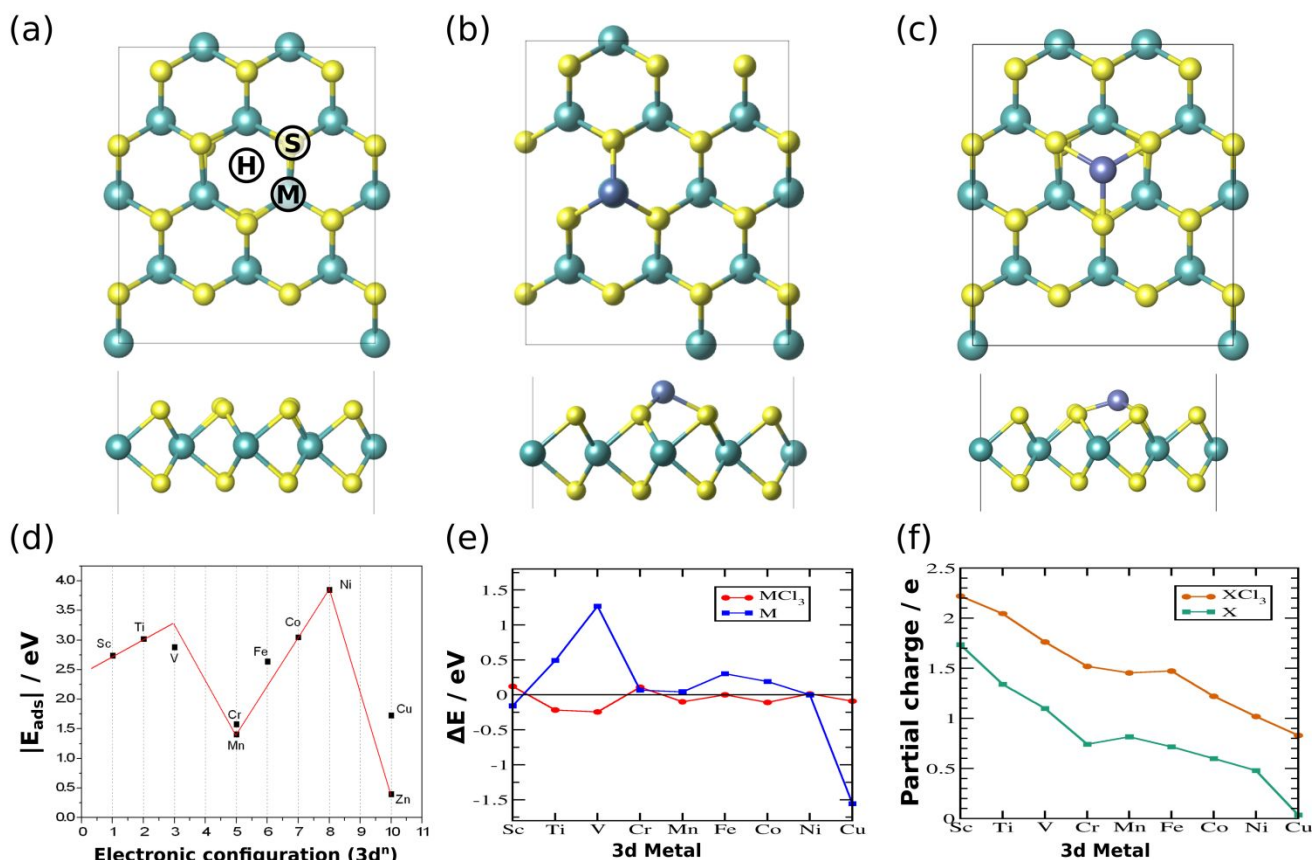


Figure 1: DFT theoretical analyses of MoS₂-TM complexes. Optimized (relaxed) structures for (a) pristine MoS₂ (possible coordination sites indicated); (b) MoS₂-Co in the M site configuration; and (c) MoS₂-Co in the H site configuration. (d) Adsorption energy as a function of the transition metal electronic configuration for MoS₂-TM complexes. (e) H- and M-site adsorption energy difference for the 3d TMs for MoS₂-TM and MoS₂-TM-Cl₃ coordination compounds. (f) Partial charge for the TMs in the cases of MoS₂-TM and MoS₂-TM-Cl₃ coordination compounds.

The electronic band dispersion was calculated to investigate the influence of TM and TM-Cl₃ coordination on the electronic properties of MoS₂. Figure 2 shows the band dispersion for MoS₂-Co-Cl₃, MoS₂-Ni-Cl₃, and MoS₂-Cu-Cl₃ on both H and M sites as well as for pristine MoS₂. We notice that for all calculated 3d TMs, the material remained with a direct gap after functionalization. However, the Fermi level energy, the states near the Fermi level, and the spin polarization of these states were drastically affected by the TM's coordinated to the MoS₂ surface (Figure 2). For example, the adsorption of Co atoms creates new states near the Fermi level, between 0 and 0.5 eV, localized on the Co atoms when the CoCl₃ complex is coordinated on the H site (Figure 2b). On the other hand, when CoCl₃ is in the M site (Figure 2c), new states appear not only near the Fermi level, but also near the conduction band (CB), positioned ~0.25eV under the CB. MoS₂→Co charge transfer transitions can lead to new optical absorptions/emissions in the visible and near-infrared spectral ranges. For NiCl₃ (Figure 2c and Figure

2f), the new levels localized above the Fermi level, at ~ 0.1 and ~ 0.75 eV, can lead to $\text{MoS}_2 \rightarrow \text{Ni}$ charge transfer transitions, corresponding to optical absorption/emission in the mid and far-infrared regions. The coordination of Cu atoms creates localized states above the Fermi level and near the valence band (VB; Figure 2d and Figure 2g) at ~ 0.05 eV and ~ 0.5 eV for the Cu coordination at the M and H site, respectively.

For the MoS_2 -TM complexes, without Cl atoms, the coordination of single TM atoms leads to new states below the Fermi level, between -1 and 0 eV, for Co and Ni, and for Co, they have different spin polarization, see Figure S1 in the Support Information. Therefore, the coordination of TM or TM-Cl_3 on the MoS_2 surface can be explored to carefully tune the TMD's optical, electronic, and chemical properties by choosing the TM and its coordination sphere. Another important aspect is that these controlled changes can be performed with minimal modifications on the crystalline monolayer since there is no significant change of the Mo-S bond length and Mo-S-Mo bond angle after TM functionalization. This is a clear advantage compared to other doping strategies, such as controlling the vacancy density or interstitial/substitutional doping, where high doping levels cannot be achieved without compromising materials stability and mechanical properties.²² Based on the DFT calculations, we see that we can perform the functionalization of MoS_2 monolayer with 3d TMs such as Cr, Mn, Co, Ni, Cu, and Zn. We can now correlate the trends of E_{ads} calculated by DFT with experimental results obtained by photoluminescence, XPS, and REELS, as we shall discuss in the following sections.

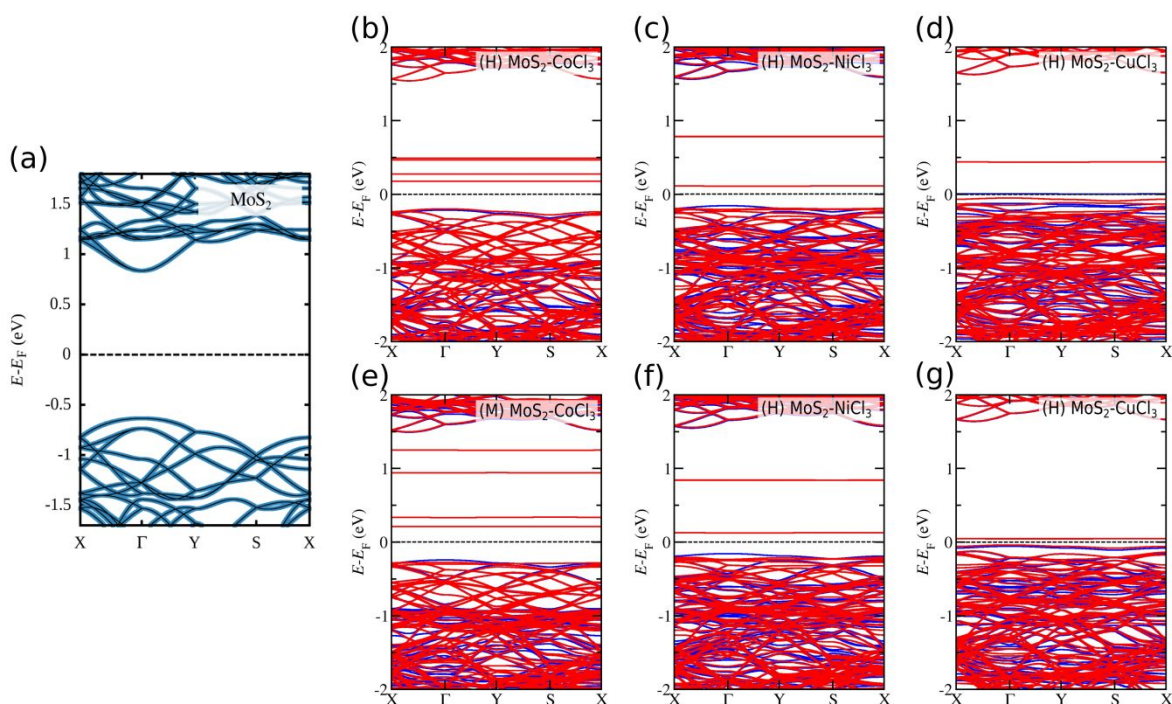


Figure 2: Electronic Band Dispersion of TM functionalized MoS₂ calculated by DFT. (a) Electronic structure of pristine MoS₂. (b-g) Electronic band dispersion of Co-, Ni-, and Cu-functionalized MoS₂ via H (b-d) and M (e-g) sites with Cl₃ completing the TM's coordination sphere. The blue and red curves indicate states with different spin polarization. The discrete "flat" levels are new states localized on the TM atoms, created after functionalization, suggesting the possibility to control the doping type by means of the TM coordination site. For all systems the Fermi level was shifted to zero.

Experimental characterization of MoS₂-TM coordination complexes

Doping of MoS₂ via TM functionalization. CVD-grown MoS₂ were characterized by Raman spectroscopy and Atomic Force Microscopy. Figure S2 a, in the Support information, shows the presence of monolayers MoS₂ with an average height of 0.72 nm. The monolayer nature of CVD-grown MoS₂ was also confirmed by Raman Spectroscopy where the difference in wavenumber of A_{1g} and E_{2g} is approximately of 21 cm⁻¹ (Figure S2 b and e).

TM coordination of MoS₂ was performed by exploring a straightforward acid-base reaction between a Lewis acid, the TM precursor, and a Lewis base, the MoS₂ surface. During the reaction, sulfur's 3p valence electrons are donated to TM's 3d valence orbital, forming an MoS₂-TM coordination bond. The functionalization reactions were performed on CVD-grown MoS₂ monolayers as described in the methods section. TM chlorides, acetates, and sulfates were chosen since they form labile complexes with TM in aqueous and ethanol solutions, favoring ligand exchange reactions on TM's coordination sphere. XPS measurements were conducted on MoS₂-TM samples functionalized in a TM solution of 1x10⁻⁴ mol L⁻¹ to confirm the TM presence on the MoS₂ surface. The high-

resolution spectra in specific regions of each TM (Figure S3) revealed the presence of the studied metals, and the chemical shift for each one can be related to its chemical environment and the chemical state. Figure 3 depicts the XPS results and indicates that TM functionalization was effective since we observed shifts on the Mo 3d and S 2p core-levels.

The TM core-level spectra were compared with known species of each TM to elucidate the obtained oxidation states, as shown in Figure S3. For Cr, its 2p core-level spectra are comparable to that of Cr_2O_3 .²³ Cr 2p orbit exhibits a multiplet splitting with a binding energy of 576.7 eV for Cr^{3+} $2p_{3/2}$ and 586.5 eV for Cr^{3+} $2p_{1/2}$, and a peak separation of 9.8 eV (Figure S3a), indicating the presence of Cr^{3+} on the MoS_2 surface. For Mn, the presence of a satellite peak indicates an Mn^{+2} oxidation state, and the spectra are comparable to that of MnO , with peaks at 641.2 and 653.2 eV for Mn $2p_{3/2}$ and $2p_{1/2}$, with a slight redshift of 0.2 eV (Figure S3b).²³ Co $2p_{3/2}$ 781.1 eV and $2p_{1/2}$ 797.1 eV peaks presented a blueshift of 1.4 eV and are comparable to CoO , with a spin-orbit splitting of 16.0 eV, and characteristics satellites, confirming the presence of Co^{2+} (Figure S3c).²³ For Ni, we observed peaks at 856.0 and 873.6 eV, assigned to $2p_{3/2}$ and $2p_{1/2}$, respectively. The Ni 2p core-level spectra are similar to $\text{Ni}(\text{OH})_2$, with prominent blueshift and spin-orbit splitting of 17.6 eV. However, the Ni $2p_{3/2}$ peak seems asymmetric and comparable to NiO , suggesting a mixture of species with the Ni^{2+} state (Figure S3d).²³ For Cu, the XPS spectra exhibit a mixture of Cu^{2+} and Cu^{1+} , since there is a satellite peak (938.0 to 947.1 eV) between the Cu $2p_{1/2}$ (952.7 eV) and $2p_{3/2}$ (932.9 eV) peaks; this peak is broad and may have contributions of both Cu^{2+} and Cu^{1+} species (Figure S3e).²³ Thus, Cu 2p core-level XPS spectra indicate a reduction of Cu^{2+} to Cu^{1+} during the MoS_2 functionalization. Further results suggest that this reduction occurs spontaneously on the MoS_2 surface (see below for details). The Zn spectrum has peaks at 1022.4 and 1045.4 eV, which are assigned to Zn $2p_{3/2}$ and $2p_{1/2}$, indicating a Zn^{2+} oxidation state. This is in good agreement with that of ZnO , showing no shifts (Figure S3f).²³

For all TMs studied here, their oxidation states remained unchanged after the functionalization, except for Cu, where the oxidation state reduced. The shifts observed on the MoS_2 XPS spectra can explain the charge transfers between the TM and MoS_2 .^{24,25} Figure 3a shows the spectra of Mo 3d core-level of pristine and doped MoS_2 . The deconvolution of the pristine MoS_2 spectrum (Figure 3c) shows the characteristic Mo^{4+} $3d_{5/2}$ peak at 230.0 eV that we will reference later for further discussion. When the MoS_2 is functionalized with a TM, charge transfer may occur, thus leading to new charge densities on Mo and TM atoms; therefore, a shift in the Mo^{4+} $3d_{5/2}$ peak is

expected. In this context, a blueshift indicates a charge transfer from Mo to the TM, leading to a more negative character on the TM and a more positive character (p-type doping) on the MoS₂, increasing the binding energy of Mo electrons. Moreover, a redshift indicates a charge transfer from TM to Mo, leading to a more positive TM and a more negative character (n-type doping) in MoS₂, thus decreasing the binding energy of its electrons.

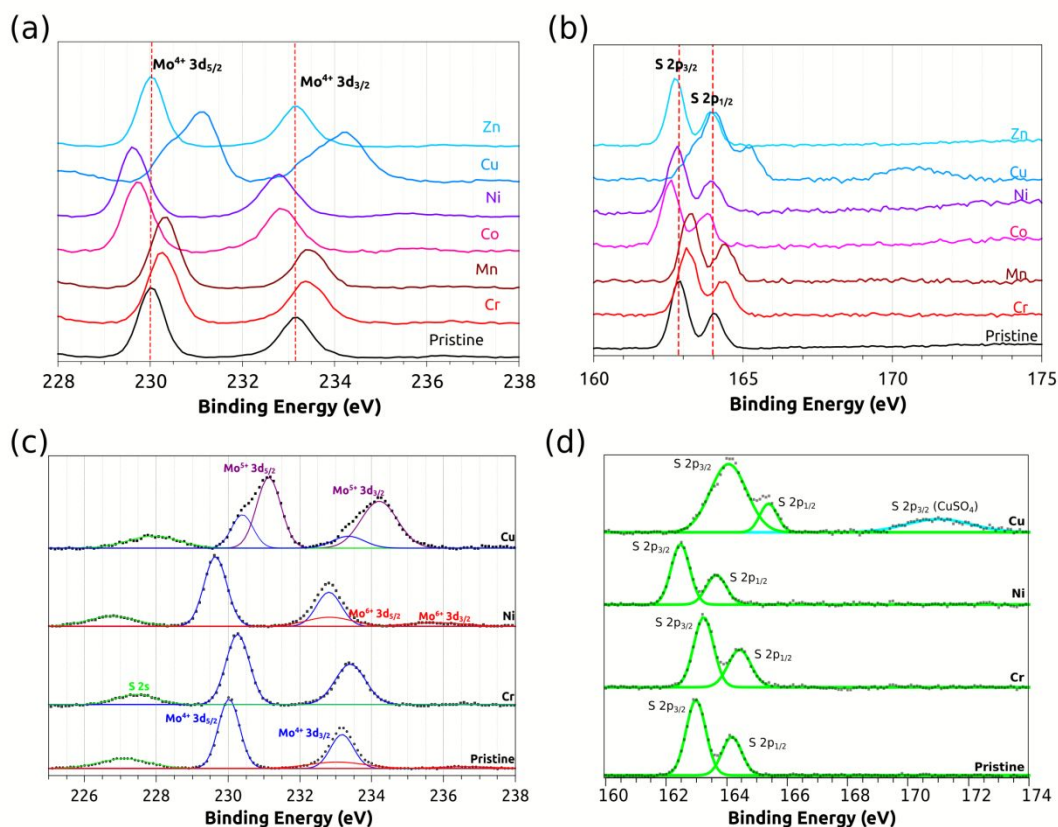


Figure 3: X-ray photoelectron spectroscopy studies of MoS₂-TM complexes. (a) XPS spectra of Mo 3d orbit on pristine and MoS₂-TM complexes. The curves are the original spectrum after C1s (284.8 eV) calibration. (b) S 2p orbit of pristine and MoS₂-TM, showing the S 2p_{1/2} and 2p_{3/2} peaks. (c) Deconvolution of Mo 3d spectra for pristine, MoS₂-Cr, MoS₂-Ni, and MoS₂-TM. The blue curves are the Mo⁴⁺ 3d_{5/2}, and 3d_{3/2}, purple curves are the Mo⁵⁺ 3d_{5/2} and 3d_{3/2} peaks, and the red curves are the Mo⁶⁺ 3d_{5/2} and 3d_{3/2} peaks. The green curves are the S 2s peak. (d) Deconvolution of S 2p spectra for pristine, MoS₂-Cr, MoS₂-Ni, and MoS₂-TM. The green curves are the S 2p_{1/2} and 2p_{3/2} peaks, and the blue curve is the S 2p_{3/2} for the CuSO₄ precursor.

The Mo 3d core-level spectra for the MoS₂-Cu samples indicate the oxidation of Mo⁴⁺ to higher oxidation states. The deconvolution of Mo 3d spectra in Figure 3c indicates the presence of Mo⁵⁺ peaks located at 231.1 and 234.2 eV. Thus, there is spontaneous oxidation of Mo⁴⁺ to Mo⁵⁺ followed by the Cu²⁺ to Cu¹⁺ reduction, as indicated by the Cu 2p spectra (Figure S3e). In Figure 3c, the deconvolution of Mo 3d spectra of pristine, MoS₂-Cr, and MoS₂-Ni samples are also presented, showing that the oxidation of Mo⁴⁺ is observed only for the Cu samples. The presence of Mo⁶⁺ in some pristine and functionalized samples is originated from Mo oxide remnants from the CVD

synthesis.²⁶ The S 2p peak in the MoS₂-Cu sample is shifted to higher energies due to the change in Mo oxidation state; however, it is still in the typical range of sulfides.²³ For all the S spectra (Figure 3b and 3d), similar behavior is observed since MoS₂ has a high degree of mixing of Mo and S atomic orbitals.²⁷

Bandgap tuning through TM coordination.

MoS₂ is a layered semiconductor that shows the transition from indirect to direct bandgap when it reaches a monolayer.²⁸ To evaluate if the bandgap remains direct after the TM functionalization and study possible shifts on the bandgap values, REELS measurements were performed. Figure 4 shows the Tauc-Plot obtained from the REELS spectra, where we can observe that the doping does not change the direct bandgap character, indicated by the linear regression on the gap transition presented. All linear regression showed an R² of 0.99. Small shifts in the bandgap value can also be observed when analyzing the linear regression and the baseline (Figure 4). In general, as we can see, TM-functionalization, except Mn and Zn, lowered the bandgap of MoS₂, indicating the creation of new states between the VB and the CB. However, due to the low energy resolution, only the shift observed for Cr and Co samples can be considered. Therefore, experiments with higher resolution are needed to fully understand the influence of TM doping on MoS₂ bandgap values. It is noteworthy that the shoulder between 1.6 and 2.4 eV can be assigned MoS₂ excitons and trions.²⁹ However, due to our energy resolution, they cannot be separated, and the TM's effects on the excitons will be discussed in the next section based on PL measurements.

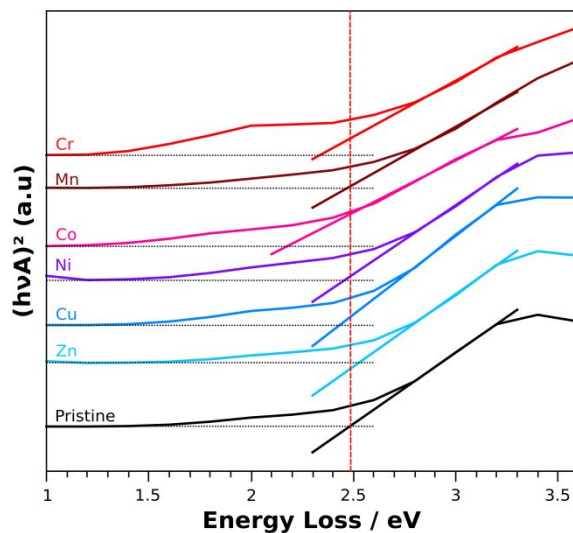


Figure 4. Tauc-Plot from the REELS data for MoS₂-TM indicated the bandgap by interception between the linear regression and the baseline. All linear regressions presented R²=0.99.

Photoluminescence tuning through TM coordination.

Optically generated electron-hole pairs in monolayer MoS₂ form stable exciton states even at room temperature because of the extremely large Coulomb interactions in atomically thin 2D materials.^{29,30} The neutral exciton plays an important role in the optical properties of the monolayer. Figure 5a shows the PL spectra for a typical monolayer with the main excitonic peak at 1.83 eV (exciton A) related to the direct bandgap transition at the K point.³⁰ PL spectroscopy measurements were carried out for MoS₂-TM complexes at various TM concentrations ranging from 1x10⁻⁹ mol L⁻¹ to 1x10⁻⁶ mol L⁻¹ to study the TM coordination's effect on the optical properties of MoS₂. Figure 5a shows the PL spectra of pristine and Ni functionalized MoS₂ monolayers. The PL intensity and shape of the A exciton are significantly altered after Ni functionalization and change as a function of TM concentration.

The PL peak can be deconvoluted and fitted by two Lorentzians, the neutral exciton (X) and the trion (X⁻), to understand these spectral changes. It can also be seen that the X⁻ peak was enhanced relative to the X intensity after Ni functionalization. The formation of the coordination π backbonds between the S and Ni atoms results in Ni electrons being transferred to the MoS₂, leading to an increase in the trion intensity relative to the neutral exciton intensity. These changes on exciton and trion populations result in an overall PL quenching and a widening due to MoS₂ functionalization, in agreement with the XPS and DFT results aforementioned.²⁹ The exact opposite effect is seen for Cu functionalization (Figure 5e). After Cu functionalization, we note an increase in the exciton intensity

relative to the trion intensity, similar to Au functionalization, resulting from p-type doping of MoS₂.¹⁶ Figures 5(b-d,f-h) further show the exciton to trion ratio for other MoS₂-TM complexes. After TM functionalization, some metal ions such as Cr, Co, and Ni significantly quench the neutral exciton and enhance the trion intensity. For Mn and Zn, we observe only a small quenching effect in the PL, which can be explained by their half shell and full shell 3d configurations.

To further verify the trends in PL spectra as a function of functionalization with the different metals, we plotted the normalized exciton to trion ratio percentage change as a function of the 3d metal concentration (Figure S4). Like that induced by Ni coordination, a high decrease in the exciton-trion ratio was also observed for Cr and Co functionalization. Since the trion has a smaller PL efficiency, the overall PL intensity decreases with the Ni, Cr, and Co doping. In contrast, for low concentrations (1.10^{-9} mol L⁻¹ - 1.10^{-7} mol L⁻¹) of Zn, practically no PL changes were observed. We notice just a small intensity (less than 20% change) decrease for Zn and Mn functionalizations. These results show a remarkable resemblance to the trend of theoretical adsorption energy shown in Figure 1 and the XPS results. As expected, Mn and Zn showed the smallest effect due to the half and closed-shell configurations, respectively, thus leading to lower stabilization energy for the 3d orbitals upon their coordination to the sulfur atoms on the surface.

In contrast, Ni and Co showed the highest effect on the PL spectra, both in intensity and exciton/trion populations. These results suggest that the effects of Ni coordination on MoS₂ were maximized by the formation of a stronger covalent Ni-S bond, which increases the charge delocalization and the possibility of ligand-metal charge transfers. It is also worth noting that the change in PL is of positive correlation between the concentration of TM ions in all cases, regardless of n or p doping types.

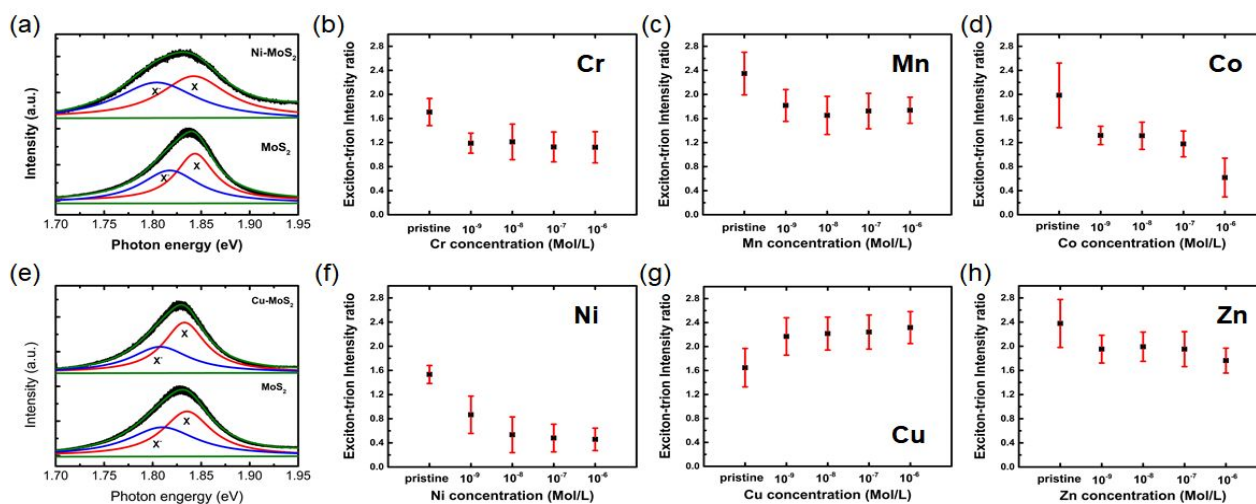


Figure 5: PL spectra analysis of TM functionalized MoS₂. (a) Photoluminescence spectrum of pristine and functionalized MoS₂ monolayers. The A exciton is deconvoluted into the trion (X-) (blue curve) and exciton (X) (red curve) peaks through Lorentzian functions, also the baseline (green curve). After functionalization, the trion intensity increased while the exciton intensity decreased, which corresponds well with the n-type doping effect of the Ni functionalization. (b) Photoluminescence spectrum of pristine and Cu functionalized MoS₂ monolayers. After functionalization, the trion intensity decreased while the exciton intensity increased, which corresponds well with the p-type doping effect of the Cu functionalization. (b-d and f-h) Exciton to trion intensity ratio of pristine and functionalized MoS₂ for different TM precursors: Cr (b), Mn (c), Co (d), Ni (f), Cu (g), and Zn (h) at different concentrations.

Morphological Characterization

In order to characterize and identify the structure of MoS₂-TM complexes, morphological characterization was performed by Optical Microscopy, SEM, HAADF-STEM, and STEM Simulation. Figure 6a shows an optical image of the MoS₂-Ni sample where triangular flakes typical of monolayer MoS₂ can be observed. We also notice some multilayer regions with higher contrast and some black points of MoO₃ residue. Even though we did not observe the formation of TM with zero oxidation state by XPS, SEM was used to evaluate the possible formation of TM-nanoparticles on the MoS₂ surface.¹³ Figure 6b depicts an SEM image of the MoS₂-Ni sample after functionalization with NiCl₂ solution at 10⁻⁴ mol L⁻¹. The MoS₂ monolayer is highlighted in yellow and, as can be seen, even with a high TM concentration, no nanoparticles were present on the flake surface, in agreement with XPS results. High-resolution HAADF-STEM was conducted to study the atomic structure of the TM atoms on MoS₂. The ADF intensity changes depend on the Z-number of atoms ($\sim Z^{1.6-1.9}$),³¹ thus, Ni atoms stand out in the MoS₂ lattice. As shown in Figure 6c, bright single Ni atoms on top of the MoS₂ lattice can be observed, similar to our previously published results on AuCl_x functionalized MoS₂.¹⁶ STEM simulation was performed using Prismatic Software to compare the line scan profile of the MoS₂-Ni. Figure 6d shows the simulated image, and

Figures 6e-f show the line scan for the experimental and simulated images, respectively. It can be observed that the contrast profile is similar in both cases. The distance between the Ni atoms is similar, 0.978 nm and 1.09 nm for experimental and simulation data. The difference in the intensity ratio between Ni atoms and the regular MoS₂ lattice, 2.16 and 1.46 for experimental and simulation data, can be related to the experimental profile's low signal/noise ratio. Despite the differences, we can clearly see the similarity between the two line scans, confirming the atomic coordination of Ni atoms to the MoS₂ surface. The imaging of other TMs studied, such as Co and Cr, were also performed, but due to their lower Z number and $|E_{\text{ads}}|$ compared to Ni, we could not identify these atoms on top of the MoS₂ lattice.

It is noteworthy that the HAADF-STEM image reveals that Ni atoms were found on the MoS₂ basal plane and not on the defect or edge regions, indicating that the Ni functionalization occurs by its coordination on the S atoms at the M site, as predicted by the DFT calculations. Additionally, experimental and theoretical STEM images prove that TM's doping of MoS₂ occurs via coordination on the TMD surface and not via the formation substitutional solutions.

To further evaluate TM coordination on the MoS₂ basal plane, PL mapping was performed on pristine and MoS₂-TM samples. The results for a MoS₂-Ni sample functionalized with Ni²⁺ solution at 10⁻⁷ mol L⁻¹ are shown in Figure S5. As discussed in the previous sections, Ni functionalized MoS₂ has decreased exciton/trion ratio and overall PL intensity since the trion has a smaller PL efficiency. Figure S5 shows that the intensity change is uniform on the whole flake, indicating that Ni coordination is homogeneous on the MoS₂ basal plane. Similarly, we observed a redshift of the PL peak due to the increase in the trion population, which was more pronounced on the flake center. Figure S6 shows Co functionalization exhibiting a similar behavior, indicating that the TM coordination is homogeneous on the entire flake.

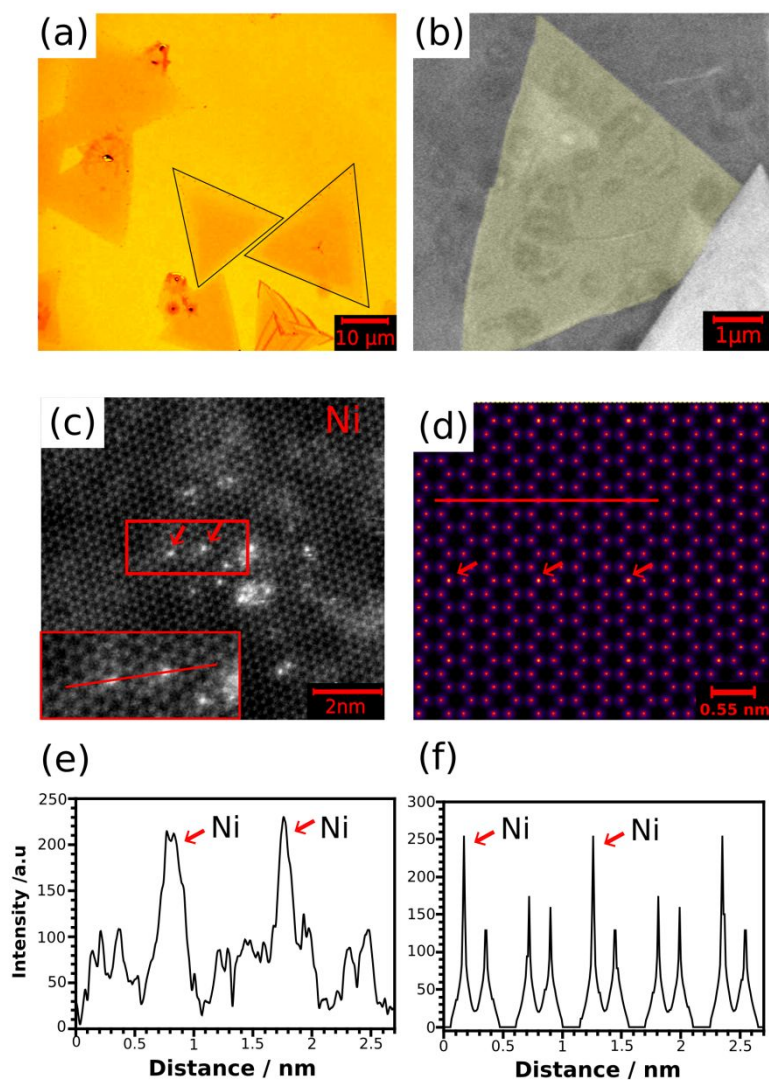


Figure 6. Imaging of MoS₂ by different microscopy techniques. (a) Optical Microscopy showing triangular MoS₂ monolayer flakes and dark spots of MoO₃. (b) SEM image of a Ni functionalized MoS₂ flake showing the absence of aggregates or Ni nanoparticles. (c) HAADF-STEM image of MoS₂-Ni, where the bright spots show Ni single atoms atomically dispersed on the MoS₂ basal plane, the inset shows where the line profile was acquired. (d) STEM simulation of MoS₂-Ni calculated from the DFT optimized structure. (e) Line scan profile of the MoS₂-Ni, the red arrows indicate where the Ni atoms are placed. (f) Line scan profile of the MoS₂-Ni simulation, the red arrows indicate where the Ni atoms are placed.

Discussion

Recently it was proposed that Classical Coordination Chemistry concepts could be applied to understand the single-atom functionalization of graphene and its derivatives.¹¹ In our previous work, we expanded this vision to explore the functionalization of MoS₂ with single Au atoms and its effect on a field-effect transistor.¹⁶ Here, coordination chemistry was applied to understand the trends observed for the coordination of 3d-TMs on the MoS₂

surface. The coordination of SA-TM on the 2DM surface can be understood as forming coordination complexes on the material's surface.¹¹ Thus, an analogy between the molecular orbital theory for coordination complexes and 2DM solid-state physics can elucidate the trends and properties observed after the TM functionalization of MoS₂ monolayers. Coordination chemistry and hard-soft acid-base concepts^{16,32,33} can lead to a greater understanding and control of the chemical, electric, and optical properties of 2D materials.

The coordination of individual atoms of transition metals on the MoS₂ monolayer was carried out by exploring ligand exchange reactions in different transition metal complexes' coordination spheres. In these reactions, one or more ligands bound to the metal, chloride or acetate, were replaced by S atoms on MoS₂, creating a covalent bond between the 2D material and the TM without rely or creating new defects in the material, Figure 7. MoS₂ can donate electron density to the metal by forming a sigma bond, using the sulfurs' p electrons in the VB. Simultaneously, the metal can donate electronic density back to MoS₂ through π back-donation involving the metal d orbital and empty states in the MoS₂ CB. Thus, depending on the TM nature, the MoS₂ system will exhibit an n or p-type doping. It is well known that CVD-grown MoS₂ contain a large number of vacancy defects (e.g., S vacancies).^{34,35} However, the TM's reactivity around a defect depends on the type of defect and the partial charge it induces in adjacent atoms. For example, if we consider a S vacancy, the TM atoms will likely not go near the vacancy because of the lower electron density.³⁵ As we demonstrated in our previous work where MoS₂ was doped with single Au atoms, the TM atoms tend to hopping from one S site to another without interact with defects on MoS₂ basal plane.¹⁶

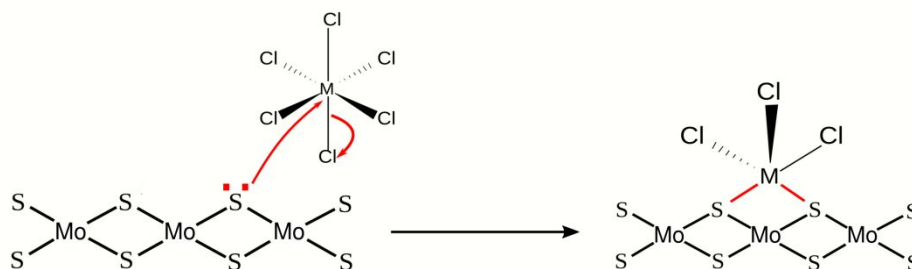


Figure 7: Reaction scheme for the coordination of transition metals on the MoS₂ surface

Classical Werner coordination complexes with closed-shell (d^{10}) and the half-shell (d^5) TM in a weak-field (low-spin) configuration do not present ligand-field stabilization energy (LFSE) due to the spherical symmetry of these electronic configurations.³⁶ In contrast, in TM with d^3 and d^8 electronic configurations, the low-energy ligand

orbitals have a higher electron population on low energy orbitals and consequently higher LFSE.³⁶ Our DFT calculations showed that TM coordination on M and H sites have very close energies when the TM's coordination sphere is complete with Cl ligands. The TM will acquire an octahedral geometry similar to *fac* isomers of TMA_3B_3 complexes in both sites, where 3 S atoms are on one triangular face and the Cl atoms on the other face. Both S and Cl atoms are π donor ligands; thus, the TM should adopt a weak-field configuration. Since the MoS_2 -TM functionalization occurred under mild conditions, we expect that the TM's coordination sphere will be composed of three S atoms and three ligands from the precursor salt, chloride, or acetate in our case. Additionally, we expect that TM coordination on MoS_2 will follow the same trend observed for the LFSE shown in Figure 8a.

The MoS_2 -TM complexes with d^{10} (Zn) and d^5 (Mn and Cr) should have smaller adsorption energy (Figure 1d). For different configurations, the non-symmetrical electronic distribution and the degeneracy loss of 3d orbitals lead to a stability gain upon the coordination, increasing the adsorption energy. As for classical coordination complexes, Ni, with d^8 electronic configuration, shows the higher adsorption energy due to the complete occupancy of the low-energy ligand orbitals.³⁶ This higher adsorption energy could explain that the MoS_2 -Ni complex was the only one that is stable during e-beam irradiation on HAADF-STEM imaging, the more significant BE shift in the XPS spectra, and the more pronounced decrease of exciton/trion ratio.

Wissam Saidi calculated the adsorption (E_{ads}) and cohesive (E_{coh}) energies for 3d metal on the MoS_2 surfaces and showed the $E_{\text{ads}}/E_{\text{coh}}$ ratio varies between 0.5 and 0.8.³⁷ Among the 3d TMs, Ni and Co have the largest ratio of $E_{\text{ads}} / E_{\text{coh}} \approx 0.8$ but are characterized with diffusion barriers of *ca.* 1 eV. Thus, it is expected that these metals could form small clusters following the Stranski–Krastanov growth model. However, in our case, the transition metals were initially adsorbed through the complexes with chlorine, where attractive interactions between functional groups to form clusters are much smaller. In addition, core-level XPS spectrum reveals that all transition metals coordinated on MoS_2 surface are cations. Interestingly, the absence of elemental transition atoms should prevent the formation of stable clusters and particles since the coordinated metals are positively charged ions that show electrostatic repulsion. The repulsion and coordination bonding resulted in stable transition metals single ions even for temperatures of 200 °C, as showed in the HAADF-STEM images of annealed samples in Figure S12.

To better visualize the observed trends on XPS, REELS, and PL, we plotted the difference between the pristine and MoS_2 -TM samples for each experimental parameter analyzed as a function of the number of electrons on d

orbitals (n). Figure 8 compares all trends with the ligand-field stabilization energy for classical coordination complexes. Figure 8b shows the binding energy shift of Mo and S core levels for MoS₂-TM samples. We can observe a blueshift for Cr, Mn, and Cu, increasing the binding energy of Mo⁴⁺ 3d electrons. For Co and Ni, a redshift was observed with ΔBE of -0.3 and -0.4 eV, respectively. For Zn, no considerable shift was observed on Mo 3d peaks. The S 2p core-level spectra indicate the same behavior observed in the Mo 3d spectra for all 3d TM studied here. This is expected since the VB's top and the CB's bottom in the MoS₂ show a high degree of mixing of Mo and S atomic orbitals.²⁷ Therefore, both S and Mo core-level spectra should exhibit similar shifts upon TM coordination. The large shift observed for MoS₂-Ni samples can again be related to Ni²⁺ higher ligand-field stabilization energy.

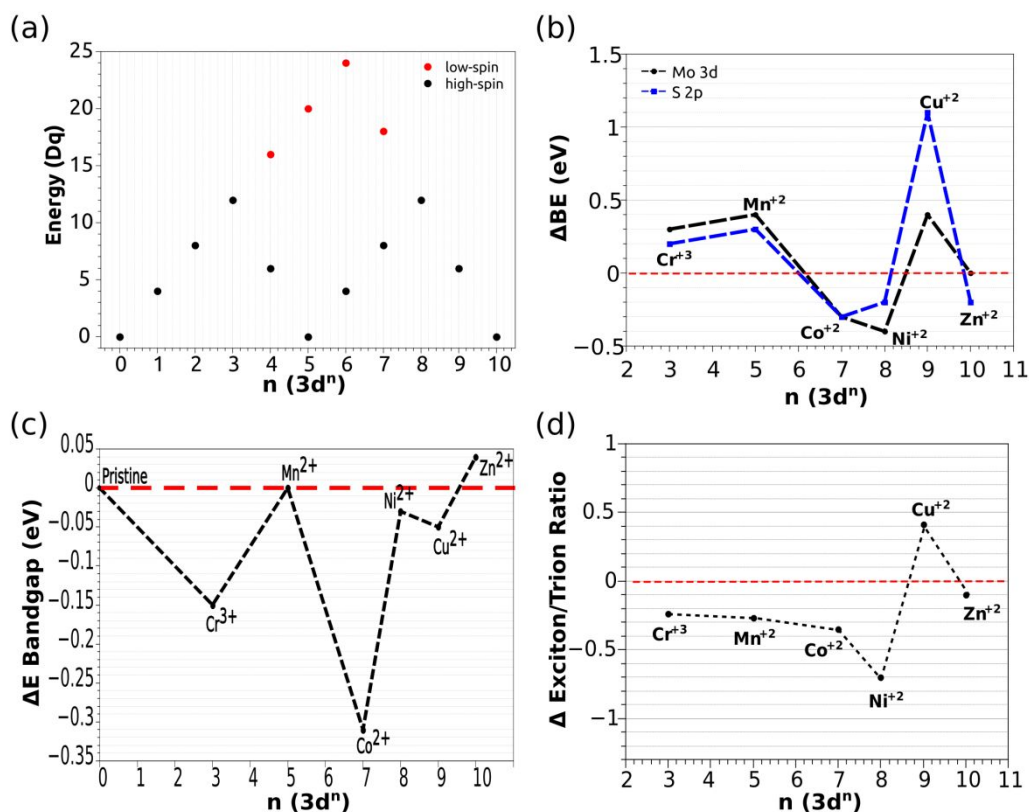


Figure 8: (a) Ligand-field Stabilization Energy for 3d TM complexes, showing the weak and strong-field configuration. The ligand-field splitting parameter Dq is equal to $Ze^2 r^4 = 6a^5$, where Z is the TM charge, e the elementary electron charge, r the TM radius, and the TM-ligand bond distance. (b) Binding energy shift for S 2p_{3/2} (blue curve) and Mo 3d_{5/2} peak as function of TM 3d electronic distribution for MoS₂-TM samples. (c) bandgap shift calculated from the Tauc-plots showed in Figure 4. (d) Normalized exciton to trion intensity changes showing the percent change in exciton to trion ratio for various TM functionalized MoS₂ samples at different TM concentrations. The TMs here can be separated into three groups. One is Cu, which shows an increase in the exciton to trion ratio, indicating p-type doping on the MoS₂. The second group is Zn, Mn, and Cr, where we see a small decrease in the ratio, indicating weak n-type doping of MoS₂. The last group is Co and Ni, where we see a large decrease in the ratio that corresponds to strong n-type doping of MoS₂.

The Pearson acid-base hard-soft theory can be applied to rationalize the direction of the BE energy shift. When the acid's LUMO level is the closest to the base's HOMO level, the acid-base coordination bond has a more covalent character, and charge transfer may occur between the species' frontier orbitals. When the acid and base valence states have a significant energy difference, the interaction between them has a more ionic character, and some electron withdrawal effects can be observed due to Coulomb interactions. For MoS₂-TM complexes, we can estimate the TM LUMO by its electron affinity, and the base's HOMO level is the top of the MoS₂ VB. In order to elucidate the observed trends on XPS spectra of MoS₂-TM samples and how each TM interact with MoS₂, the energy level diagram shown in Figure 9 was created using the HOMO and LUMO orbitals of each TM, estimated

by the ionization potential and electron affinity of the neutral TM, the $\text{TM}^{2+}/\text{TM}^{1+}$ redox potentials,³⁸ and the absolute energies of MoS_2 VB and CB.³⁹ Although the HOMO and LUMO TM's energy levels are referenced to the +1 oxidation state, and the XPS results indicate +2 oxidation states, we expected these energy levels to be lower. However, the same trend is expected, and it is comparable to the experimental data.

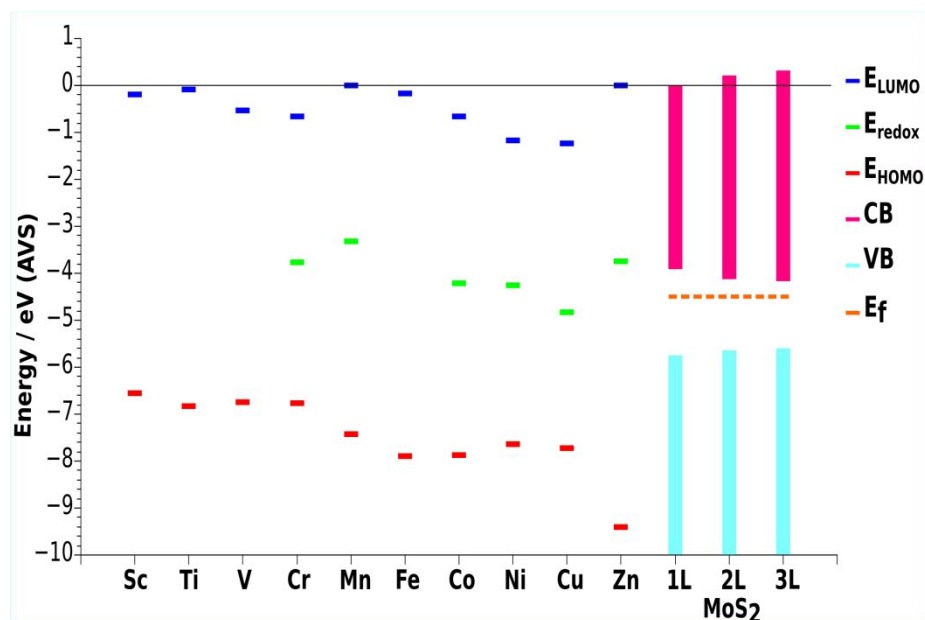


Figure 9: Diagram of HOMO and LUMO energy of the first-row transition metals and energy values of electronic bands of MoS_2 in absolute vacuum scale. The red lines indicate HOMO energy of TM, and blue lines indicate LUMO energy of TM, green lines indicate the redox potential of the TM pairs, light blue boxes represent the valence band of MoS_2 , pink boxes represent the conduction band of MoS_2 , and dot-dashed orange line indicates the Fermi Level of MoS_2 .

Due to the small energy difference between the MoS_2 VB and CB, we can consider it as a soft base (Absolute Hardness – $\eta \sim 0.9$),¹¹ which will interact better with a soft acid. The fact that TM LUMO is relatively close to MoS_2 VB leads to a more covalent bond and a higher probability of a charge transference from MoS_2 to the TM. This behavior can be observed for Cr, Mn, Co, and Ni. This leads to the formation of MoS_2 -TM coordination complexes with strong sigma covalent bonds, where S atoms act as a sigma donor ligand. Mn has an intermediary acid character ($\eta = 3.72$) and induces a decrease in the electron density of MoS_2 , shifting the Mo 3d peaks towards higher energies. Meanwhile, Cr is a softer acid ($\eta = 3.05$) and tends to form a more covalent σ bond with S atoms,

and the electrons on the MoS₂-Cr bond should be more delocalized. Additionally, S atoms can act as π donor ligand, thus increasing the charge transfer to the TM and the observed blueshift on the XPS Mo spectra.

It is noteworthy that Co and Ni show a more donating character. Both are acids with intermediary hardness (η of 3.6 and 3.2, respectively) and tend to form strong covalent bonds with S ligands due to their high ligand-field stabilization energy. Due to their filled 3d orbitals, Co and Ni complexes are known to form π back-bonds with soft ligands.⁹ For MoS₂-Ni and MoS₂-Co complexes, there is a σ donation from S to TM and a π back bonding involving the 3d_{xy, xz, yz} TM orbitals to empty orbitals on the MoS₂ CB. The redshift observed on the Mo 3d core-level indicates that the charge transfer from Ni or Co to the MoS₂ is due to the more efficient back-donation. Additionally, this high degree of π back-bonding can increase the trion population, explaining the observed trend on the exciton/trion ratio shown in Figure 8d. Since Co has smaller E_{ads} than Ni ($\sim 1\text{eV}$), a higher Co concentration is needed to reach a similar exciton/trion ratio (Figure S4).

However, Co and Ni exhibit very different behavior when analyzing the bandgap shift in Figure 8c. MoS₂-Co samples displayed a bandgap shift of approximately 0.3 eV, while MoS₂-Ni samples showed no observable shift. By looking at the electronic band dispersion in Figure 2, we notice that MoS₂-CoCl₃ on the M site has a new state localized on Co atoms at ~ 0.25 eV above the VB. This new state can generate a MoS₂ \rightarrow Co charge transfer transition with energy close to the bandgap transition. Since our REELS measurements do not have enough resolution to distinguish both transitions, we observed an overall bandgap reduction. For MoS₂-CoCl₃ on the H site or for MoS₂-Co (Figure S1), there are no new levels near the VB and no new transitions should be observed on the visible region. Thus, the bandgap decrease observed for MoS₂-Co samples could indicate Co coordination on the M site and the Cl presence on its coordination sphere. For MoS₂-NiCl₃ complexes, the DFT calculations indicated the existence of midgap states, and the electronic transition from the VB to these states should occur around 0.9 eV. This transition is close to the elastic peak on the REELS spectra and cannot be observed, which leads to no changes in the MoS₂ bandgap energy. Optical absorbance measurements conducted in MoS₂ before and after the functionalization with Ni, can provide some information that can be correlated to the band structure. Figure S10 A depicts the average spectra of 10 pristine (black) and MoS₂-Ni with two Ni concentrations (red – 10⁻⁸ M and green – 10⁻⁷M). There is a small red-shift of the A and B excitons absorption peak, and an increase in the absorption in low photon energies (1.4 – 1.7 eV) that can be related to new charge transfers transitions between

localized states in the Ni atoms and the MoS₂ levels. We observe a very low signal in the Cl 2p spectra from the XPS of MoS₂-NiCl₃ and MoS₂-CoCl₃ (Figures S7 and S8). By comparing the peak area of Ni 2p or Co 2p peaks with the Cl 2p peaks as well as considering the relative atomic sensitivity factors (4.5 for Ni, 3.8 for Co, and 0.73 for Cl) of XPS⁴⁰ (Tables S2 and S3), we find that the overall atomic ratios of Ni:Cl and Co:Cl are close to 1:3. As discussed earlier, the presence of Cl anions on TM coordination sphere could prevent the cluster formation. Thus, to investigate the stability of Ni-MoS₂ samples we annealed them at 50, 100, and 200 °C and measured their opto-electronic properties and morphology after the annealing process. Figure S11 shows the PL spectra of annealed Ni-MoS₂ samples. The samples annealed at 50 °C exhibited PL intensity, excitation/trion ratio (0.4), and FWHM (330 meV) similar to the samples at room temperature, showing that the effect of Ni coordination on MoS₂ remains at temperatures up to 50 °C. For samples annealed at 100 and 200 °C, the PL intensity, exciton/trion ratios (close to 1.6), and FWHM (280 meV) were similar to the pristine MoS₂. HAADF-STEM images of the annealed samples also indicated that single Ni atoms are still observed for the three temperatures (Figure S12). However, some clustering processes can also be observed, suggesting that the effect of a single adatom is lost at a temperature higher than 100 °C due to metal cluster formation.

Zn is the hardest TM in this series ($\eta = 4.72$), so there is a poor overlapping between the Zn orbital's and MoS₂ orbital's, resulting in no variation of the Mo 3d binding energy from the XPS spectra. Additionally, due to the Zn electronic configuration of 3d¹⁰, Zn complexes do not show ligand-field stabilization energy. Hardness and ligand-field stabilization energy both contribute to the Zn's poor interaction with softer ligands. Sulfur atoms in MoS₂ can be considered a soft base, leading to a small BE shift and a slight decrease in the exciton/trion ratio in MoS₂-Zn samples. For these samples, new low energy transitions were not observed in the optical absorbance measurements (Figure S10), pointing to a small interaction between MoS₂ and Zn.

For MoS₂-Cu complexes, by comparing Cu HOMO-LUMO levels with MoS₂ VB-CB energies, we expected a more covalent interaction, albeit with a smaller E_{ads} , as shown in Figures 7 and 8⁴¹. However, looking at the TM's redox potential, we notice that Cu has a more negative value, and it is the only one below the MoS₂ Fermi level. Thus, electrons on MoS₂ can be transferred to Cu spontaneously, reducing it from Cu²⁺ to Cu¹⁺. A similar reduction effect was also reported in our previous paper that Au³⁺ could be spontaneously reduced to Au¹⁺. It is noteworthy that we could not discard the possibility of Cu⁰ formation; however, we did not observe Cu⁰ in the XPS or

nanoparticle formation on SEM images. On the other hand, Cu^{1+} does not have ligand-field stabilization energy due to its $3d^{10}$ configuration. However, due to the absence of Jahn-Teller distortions and its softer character, the MoS_2 -Cu bond energy should be higher than in Cu^{2+} and Zn^{2+} cases. These electron transfers from MoS_2 to Cu can lower the MoS_2 E_F , explaining the very high BE shift observed on Mo 3d XPS spectra. The high BE shift could also be pointing to the Mo^{4+} oxidation into Mo^{5+} . However, Raman spectra of MoS_2 -Cu samples (Figure S9) do not show any shift or new peaks when compared to the pristine samples. Therefore, we believe that Cu can induce a high degree of p-type doping on MoS_2 , which can be supported by the decrease in the trion population and the increase in the exciton/trion ratio (Figure 8d).

Conclusions

In this work, we successfully prepared TM- MoS_2 coordination complexes for 3d transition metals (Cr, Mn, Co, Ni, Cu, Zn) and demonstrated that Ni forms single atoms that are bonded to S atoms via coordination bonds. This novel approach does not rely on defects or atoms substitution and yet implies a significant impact on the optical and electrical properties of the functionalized monolayer MoS_2 . The formation of the coordination complexes led to the transfer of electrons between MoS_2 and the transition metal, which can introduce both n- and p-type doping to MoS_2 , depending on the transition metal used. Moreover, the degree of n and p-type doping can be fine-tuned by choosing the transition metal and by varying the transition metal precursor concentrations, thus controlling the electronic band structure of MoS_2 and the exciton to trion relative population. In addition, the properties of the TM functionalized MoS_2 display a trend based on the 3d electron configuration of the transition metal that matches the periodic trend of well-studied coordination compounds. This trend can serve as a guide for future chemical functionalization reactions of monolayer TMDs. The synthesis of single atoms introduced in this work could also be exploited in other applications such as single-atom catalysis (SAC), quantum information devices, optoelectronics, and enhanced sensing.

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Author contributions: The manuscript was written through contributions of all authors. H.L., W.C.S., and D.G. conducted the functionalization experiments and characterizations. L. S. G. S., A. G. V. and M. L. M. R. conducted the XPS and REELS measurements and analysis. L.S. performed the first-principle calculations. E.K. and K.T. synthesized the pristine MoS₂ materials. K.F., T.Z. and F.Z. helped with TEM characterization and simulation. Y.L. and Z.Y. provided guidance and helped analyze the data. D.G., M.T., and C.J.S.M. supervised the whole work. All authors gave approval to the final version of the manuscript. H.L., W.C.S. contributed equally.

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