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Insights into the Multifunctional Applications of Strategic Co doped MoS$_2$ Nanoflakes

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Abstract

Simultaneous tuning of magnetic, transport and electrochemical properties through strategical doping of cobalt (Co) ions in hydrothermally treated multi-layered MoS$_2$ nanoflakes (NFs) without having a secondary phase has been regarded as cutting-edge research. In our study, we have successfully incorporated Co into MoS$_2$ NFs in various percentages (0%, 2%, 4%, 6%, 8%) with significant presence of defects, strain and sulfur vacancies, rendering to prompt transformation of the surrounding 2H-MoS$_2$ local lattice into a trigonal (1T-MoS$_2$) phase. Effective amplification of magnetic property (ferromagnetic coupling on the scale of $p_{\text{eff}} \sim 4.37 \mu_B$) in 8% Co-doped MoS$_2$ NFs has been evidenced from VSM measurement. The key reasons are probably attributed to the doping induced 1T phase, the presence of zigzag edges well-established from TEM and Raman measurements, and exchange interactions between ferromagnetically ordered sulfur vacancy, Mo$^{4+}$ and Co$^{2+}$ ions. The observations obtained experimentally on magnetic measurements have been fitted well with the well-known density-functional theory (DFT) computation. Further, the effect of intentional doping on transport property has been evaluated by employing Four probe linear geometry set up. The increased carrier concentration and decreased resistance result in improved transport properties. Various transport models such as variable range hopping (VRH), nearest neighbour hopping (NNH) of the Co-doped MoS$_2$ systems have been successfully fitted in different temperature regimes with a tunable temperature coefficient of resistance (TCR) $\sim 3.0 \times 10^{-2}$ K$^{-1}$. Additionally, electrochemical measurements revealed a significant increase in electrochemical activity with
the highest proportion of Co doping (8% Co), which is likely due to increased defect levels and active surface area with expanded interlayer separation, as well as exposure of the electrochemically more active metallic (1T phase) Mo atoms in the edge planes. Therefore, our approach in achieving mixed-phase defect-rich (1T and 2H) Co-doped MoS$_2$ NFs exhibiting room-temperature ferromagnetism, high TCR and improved electrochemical performance enables it to work as an excellent multifunctional candidate in spintronic, infrared (IR) detecting and energy storage devices.

**Keywords:** MoS$_2$ nanoflakes, 1T and 2H phase, ferromagnetism, variable range hopping, hydrothermal technique, temperature coefficient of resistance, electrochemistry.

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1. Introduction

Molybdenum disulfide (MoS$_2$), as one typical candidate of graphene analogues and a member of the transition metal dichalcogenides (TMDs), has recently drawn tremendous attention in a wide range of novel applications in field-effect transistors$^1$, flexible devices$^2$, digital electronics$^3$, nano-and Opto-electronics$^{1,4}$ as well as in basic research$^{5-7}$ due to having its unique electrical, optical, mechanical and electronic properties. Based on the demanding application of diluted magnetic semiconductors (DMS), manipulating the magnetic properties of MoS$_2$ nanoflakes is crucial for expanding their applications in nanoelectronics and spintronics. However, pristine MoS$_2$ nanoflakes are intrinsically nonmagnetic. Therefore, the realization of stable magnetism in MoS$_2$ is highly desirable.

Motivated by the potential applications and the great demands for magnetic MoS$_2$ nanostructures, a variety of methods have been developed and explored in past few years. However, there are many effective ways in which the magnetism of 2D materials can be realized such as, with the introduction of defects,$^{8,9}$ surface functionalization (i.e., hydrogenation),$^{10}$ cutting 2D nanoflakes into one-dimensional (1D) nanoribbons (NRs),$^{11,12}$ and the transition-metal (TM) doping.$^{13}$ Moreover enormous ferromagnetism in MoS$_2$ nanoflakes requires the introduction of a large number of defects which in turn results in the reduction of carrier mobility because of the formation of scattering centres or charge-trapping sites in the MoS$_2$ sheets. Although surface functionalization is capable of producing stable magnetism, experimentally it faces a big challenge. For example, surface hydrogenation requires the implementation of external stress in MoS$_2$ nanoflakes. The introduction of ferromagnetism in MoS$_2$ NRs is very crucial and its edge type needs to be well-controlled as the zigzag NRs are ferromagnetic whereas armchair NRs are nonmagnetic. Structure and vacancy-related ferromagnetism contributed from zigzag edges of MoS$_2$ nanoribbons and sulfur vacancies in MoS$_2$ flakes have been reported in several theoretical calculations.$^{11,14,15}$ In
this regard, TM doping is a facile and conventional way to achieve stable magnetism in 2D semiconductor materials. Moreover, the magnitude of magnetism and the dopant concentration of MoS$_2$ nanoflakes can be controlled in the doping process. Ferromagnetism in layered TMDs via substitutional doping of magnetic 3d transition-metal atoms has been reported by Ramasubramaniam et al.\textsuperscript{16} and possible ferromagnetism in MoS$_2$ by single absorption of Co atom has been claimed by Chen et al.\textsuperscript{13} first time. Evidence of room temperature ferromagnetism in Mn, Fe, Co and Ni-doped MoS$_2$ in monolayer and bulk form, initiated by substitutional defects and defect complexes have been reported by Wang et al.\textsuperscript{17} Additionally, proton beam irradiation\textsuperscript{8} and doping with nonmetal elements\textsuperscript{18} are considered to produce ferromagnetism in few-layer non-magnetic MoS$_2$. It has been shown in previous studies that localized nonbonding 3d electrons of TM atoms produce charge polarization in TM substituted 2D systems.\textsuperscript{19–21} The extra nonbonding valence electrons present in TM metal ion compared to Mo contributes magnetic moment with substitutional doping in layered materials. For example Mn-MoS$_2$ = 1 $\mu_B$, Fe-MoS$_2$ = 2 $\mu_B$, Co-MoS$_2$ = 3 $\mu_B$, Ni-MoS$_2$ = 4 $\mu_B$, Cu-MoS$_2$ = 5 $\mu_B$ moments possess 1, 2, 3, 4 and 5 extra electrons in nonbonding orbitals\textsuperscript{22}. It is worth noting that a maximum of 5 electrons can only be accommodated by 3d orbital in the single-filled states. Hence, based on the above theory, the magnetism of the TM doped MoS$_2$ structure can be tuned successfully by the internal TM engineering which plays a crucial role in the functionalization of MoS$_2$ nanomaterials in possessing defined magnetic moment. However, Co being a member of the transition metal ion group possesses a comparable ionic radius (0.70 Å) as to molybdenum (0.68 Å). Doping of Co- ion in MoS$_2$ NSs can effectively modulate structural properties by introducing vacancies, defects and strain which are also responsible for the ferromagnetism. The magnetism in MoS$_2$ nanostructures can be much influenced by the zigzag edges, while the experimental and computational study has shown that the magnetism in Co-doped MoS$_2$ nanoflakes is sensitive to the edges as well.\textsuperscript{23} Theoretically it has been shown that
Co substitution at the Mo site leads to spin-polarized state\textsuperscript{24} contributing three electrons in 3d orbital in the single-filled states. The partial replacement of Mo with the transition metals like Co creates the magnetism in MoS\textsubscript{2} which enables it as a suitable candidate as a new kind of diluted magnetic semiconductor.

Moreover, other effects such as coupling between the adjacent layers are known to stabilize the magnetism and can enhance the overall magnetization originating from the grain boundaries.\textsuperscript{25} The ferromagnetic signal was attributed to localized electronic states at grain boundaries in other nonmagnetic layered systems such as graphite.\textsuperscript{26} Even though, the interlayer coupling might be enhancing the ferromagnetic signal, such coupling is not a necessary condition for the existence of ferromagnetism as the presence of zigzag edges is sufficient and magnetization measurements certainly probe the magnetization originating from zigzag edges.\textsuperscript{11,27} Nevertheless, studies on the tuning of magnetic and transport properties of MoS\textsubscript{2} simultaneously obtained by doping of transition metal (TM) atoms are extremely critical in experimental work.

In earlier reports, it has been shown that n-type MoS\textsubscript{2}-based field-effect transistors (FETs) face limitations in certain applications due to having high contact resistance. However, to reduce contact resistance, metallic MoS\textsubscript{2} with a lithium-solution treatment has recently been introduced\textsuperscript{28,29} which is dissimilar to the conventional methods, such as chemical doping and ion implantation, used for the reduction of contact resistance in other devices. Li-treatment of MoS\textsubscript{2} results in the coexistence of various MoS\textsubscript{2} phases and consequently develops significantly different electronic and magnetic properties.\textsuperscript{30,31} Kim \textit{et al.} reported the transport properties of Li-ion treated polymorphic MoS\textsubscript{2} with a large temperature coefficient of resistance (TCR), enabling efficient IR detection at room temperature.\textsuperscript{32} Meanwhile recent studies on transport suggest that few factors such as charged impurities\textsuperscript{33–35} and localized states\textsuperscript{34,36,37} play a crucial role in controlling the dominant scattering processes that limit the carrier
mobility in mechanically exfoliated samples, and it remains unexplored. Recent studies on CVD-grown MoS$_2$ suggest that the contact resistance due to Schottky barriers needs to be carefully taken into account. The adverse impact of dominant scattering processes that limit the carrier mobility, should be critically evaluated.$^{38,39}$ The advantage of incorporation of 1T metallic phase in semiconducting 2H phase through Li-ion treatment or TM ion doping is that it controls the junction barrier resistance in TMD-based devices. In this work, we investigate the nature of various dominating charge transport mechanism which comes into play in the high and low-temperature region of multi-layered undoped (0% Co) and various amount of cobalt (2% Co, 4% Co, 6% Co and 8% Co) doped MoS$_2$ nanoflakes. Doping-induced sulfur vacancies (SVs) and cobalt dopants act as electron donors and induce localized states in the band gap leading to the narrowing of band gap$^{40}$. In undoped MoS$_2$ the electron transport is dominated by thermally excited nearest-neighbour hopping (NNH) throughout the entire temperature region (50 K-300 K) due to a lack of doping-related defects induced localized electrons. The localized electron transport in cobalt doped MoS$_2$ sample is dominated by thermally excited NNH from moderate to high temperature and variable-range hopping (VRH) dominating at sufficiently low temperatures, respectively. In this report, doping-induced ferromagnetism by cobalt ion doping in MoS$_2$ nanoflakes has been explored and verified both experimentally (VSM, EPR) and theoretically (DFT). Additionally, presence of zigzag edges has been verified by TEM measurement corresponding to 8% Co-doped MoS$_2$ NFs which probably gives rise to the ferromagnetic behaviour synergistically in association with the doping effect. The ferromagnetic behaviour of 8% Co-doped MoS$_2$ NFs having saturation magnetization ($M_s$) $\sim$1.2 emu/g and coercivity $\sim$ 70 Oe at 5 K have been observed. The role of substituted Co dopant and doping induced 1T phase upon the rising nature of ferromagnetism has been explained through the bound magnetic polaron (BMP) model. According to the BMP model, only those nearby Mo$^{4+}$ ions in 1T phase and Co$^{2+}$/Co$^{3+}$ ions in octahedral geometry
located within the effective radius of the same polaron (around a sulfur vacancy center) could interact with each other ferromagnetically giving rise to ferromagnetism in 1T@2H-MoS$_2$ nanoflakes. A detailed first principle DFT study on undoped and cobalt doped systems reveals the increasing nature of ferromagnetism assuming substitutional Co doping in pure 2H MoS$_2$ matrix. Therefore, we have successfully incorporated zigzag edges, defects and vacancies in a controlled way by doping Co in MoS$_2$ NFs while improving its electrical properties.

Layered TMDs, such as MoS$_2$, have proven their efficacy in the electrochemical energy storage/conversion field, owing to their large surface area that allows the maximum exposure of surface active sites, high mechanical strength, and flexibility in the atomic scale dimension.$^{41}$ The heterogeneous electron transfer (HET) on the edge planes of MoS$_2$ is predicted to be higher than the basal planes, thus the edge sites are more catalytically and electrochemically active than those of their basal planes.$^{42}$ Hence, it is always encouraged to fabricate MoS$_2$-based electrodes with the edge-exposed surface rather than the basal planes, of which the former improves the catalytic and electrochemical performances.$^{43,44}$ Moreover, the electrical conductivity of MoS$_2$ is another key factor that influences their catalytic and electrochemical performance. Our strategy of systematic Co-doping in MoS$_2$ increases the number of active sites in the edge planes enhances the conductivity by introducing the metallic 1T phase and increases interlayer separation aiding in the intercalation of ions easily and defects states with modulation of the band gap. Such salient features facilitate the Co-doped MoS$_2$ to function as a better electrode material (~1.7 times higher specific capacitance observed in 8% Co doped MoS$_2$ compared to the undoped one) having an improved charge storage mechanism. Our work provides a detailed investigation of the manipulation of magnetic property in achieving room-temperature ferromagnetism and transport property by varying Co ion dopant in MoS$_2$ NFs introducing 1T phase, defects, controlling edge with simultaneous enhancement in electrochemical property for future application in energy storage devices.
2. Experimental details

2.1. Chemicals used

High purity (99.9% purity) chemicals, like sodium molybdate dihydrate (Na$_2$MoO$_4$.2H$_2$O), thiourea (CH$_4$N$_2$S), cobalt acetate tetrahydrate (CO(CH$_3$COO)$_2$.4H$_2$O) were procured from Sigma-Aldrich. All the reagents are analytical reagent grade and used without further purification.

2.2. Synthesis of ultra-thin Co-doped MoS$_2$ NFs

The undoped and various percentages of Co-doped MoS$_2$ NFs were synthesized using the facile one-step hydrothermal technique using Na$_2$MoO$_4$.2H$_2$O, Co (CH$_3$COO)$_2$.4H$_2$O and CH$_4$N$_2$S as starting reagents. In a typical preparation process, 2 mmol of Na$_2$MoO$_4$.2H$_2$O and 5 mmol of CH$_4$N$_2$S were taken, dissolved into 40 mL of deionized water adjusting the pH value of the solution at 5.0 by adding 0.02 mol/L of acetic acid (CH$_3$COOH). Then the mixed solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave for hydrothermal treatment at 200 °C for 24 h and cooled down to room temperature naturally. MoS$_2$ in the form of black powder was obtained by centrifugation at 3000 rpm for 10 min. Then the black powder was washed with deionized water and ethanol several times and dried in the vacuum oven at 60 °C for 12 h. For the synthesis of 2 at. wt.%, 4 at. wt.%, 6 at. wt.% and 8 at. wt.% cobalt doped MoS$_2$ NFs, the two precursors Na$_2$MoO$_4$.2H$_2$O and Co (CH$_3$COO)$_2$.4H$_2$O were taken in the consecutive mmol ratio of 0.98:0.02, 0.96:0.04, 0.94:0.06 and 0.92:0.08 keeping the same CH$_4$N$_2$S amount in the aqueous solution and the rest synthesis process was repeated.

The MoS$_2$ NFs with various amounts of cobalt doping (0 at. wt.%, 2 at. wt.%, 4 at. wt.%, 6 at. wt.% and 8 at. wt.%) were labelled as undoped, 2% Co, 4% Co, 6% Co and 8% Co, respectively.
2.3. Characterization techniques

The instrumental specifications of X-ray diffraction (XRD), Raman measurement, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) techniques to understand the existing crystalline phase and different vibrational modes present in our samples were already reported\(^4\). The room temperature EPR spectra of the samples were recorded using an X-band Bruker ELEXSYS 580 EPR spectrometer with 9.8492 GHz of X-band frequency. The Vibrating Sample Magnetometer (VSM) in the model Lake Shore cryotronics USA, 7400 series was used to measure the magnetic property by measuring M vs H (applied field ~ -2T to +2 T) and M vs T plot (10 K- 300 K, 500 Oe). The characterization of the transport property of the samples was carried out using a Lakeshore Four-probe linear geometry set up using a low-temperature closed-cycle helium refrigeration cryostat. The powder form MoS\(_2\) samples with various amounts of Co dopants were pelletized and conducting silver contacts were made for transport property measurements.

2.4. Electrode preparation

Electrochemical measurements like cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and ac impedance studies were performed using CHI600E Electrochemical Workstation, manufactured by CH Instruments (USA) at room temperature, containing glassy carbon electrode loaded with undoped and Co-doped MoS\(_2\) samples, Ag/AgCl (in standard 3M KCl aqueous solution), and Pt electrodes as the working electrode, reference electrode, and counter electrode, respectively, using 1 M Na\(_2\)SO\(_4\) aqueous solution as the electrolyte. Before starting of all the measurements, the bare glassy carbon electrode (GCE, dia. 3 mm) was polished mechanically with 1, 0.3 and 0.05 μm alumina slurries sequentially to obtain a mirror finish, and then washed with acetone, ethanol and DI water thoroughly. The slurry was the mixture that consists of the active material, activated carbon, and poly (vinylidene fluoride) binder in a weight ratio of 80:15:5 with N, N-Dimethylformamide as solvent. Then, the slurry
was drop casted on the GCE surface carefully in a certain amount. Finally, the electrodes were dried at 80 °C for 12 h in vacuum.

2.5. Computational details

To elucidate the impact of Co dopants on the magnetic properties of MoS$_2$ nanoflakes, First-principles calculations have been performed using Vienna Ab-initio Simulation Package (VASP)$^{45}$, within the generalized gradient approximation (GGA)$^{46}$ considering the Perdew–Burke–Ernzerhof (PBE)$^{46}$ parametrization to describe the exchange-correlation interaction. The cut-off energy for the plane-wave basis set was set at 450 eV in all the computations. The relaxation convergence of energy is taken to be less than $1.0 \times 10^{-6}$ eV and all the atoms were allowed to relax using a conjugate gradient scheme until the inter-atomic forces fall below 0.01 eV/Å. All the structural optimizations and the scf calculations were done using a well-converged Monkhorst-Pack $^{47}$ $11\times11\times11$ and $21\times21\times21$ k-point grid, respectively. The electronic structure calculations were done with a much denser k-point mesh. In our calculation, we assume unit cells have 2H atomic arrangements as the 2H phase is seen to be dominant over the 1T phase in all cases. To account for Van der Waal’s interaction between two layers of the unit cell, the DFT-D2$^{48}$ method as implemented within VASP is adopted in all calculations.
3. Results and discussions

3.1. XRD Data analysis

The XRD patterns of the undoped and various percentages of cobalt-doped MoS$_2$ nanostructures recorded over the 20 range of 10$^0$-70$^0$ had been shown in our previous research paper$^{40}$. Here the XRD peaks of all undoped and Co-doped samples exactly match with hexagonal MoS$_2$ having identical peak positions. The XRD graphical plot of the samples with JCPDS card no.- 00-037-1492 is shown in Fig. 1 (a). The signature of diffraction peak corresponding to 1T phase (Supplementary information, Fig. S1) is more prominently observed in the XRD pattern of 8% Co-doped MoS$_2$ compared to other low concentration Co doping. This peak shifts to a lower angle 10.6$^\circ$ to 10.5$^\circ$ when the Co dopant percentage is increased from 2% to 8%, possibly due to the appearance of tensile strain within the lattice. The slight shift of the main (002) diffraction peak to a lower angle and increased lattice parameters (a and c) confirms the existence of uniaxial lattice strain (tensile) appearing in the lattice due to substitutional Co doping.$^{49}$ The undoped and Co-doped MoS$_2$ nanoflakes XRD pattern was successfully refined with a 2H- MoS$_2$ phase (P63/mmc, a = 3.14 Å, b = 3.14 Å, c = 12.53 Å, $\alpha$ = 90$^\circ$, $\beta$ =90$^\circ$, $\gamma$ = 120$^\circ$) having no extra crystalline impurity phase. The lattice parameters as obtained after refinement are found to be a = 3.158 Å, b = 3.158 Å, c=12.815 Å for undoped and a = 3.174 Å, b = 3.174 Å, c=12.879 Å for 8% Co-doped MoS$_2$ NFs. The refined lattice parameters agree well with previous literature.$^{50}$ The average crystallite size of all the MoS$_2$ NFs varies from 8 nm - 6 nm. It has been observed that the crystallite size as obtained by using the Scherrer formula, has decreased with the increase of cobalt dopant amount. This can be assigned to the possible appearance of lattice strain and defects induced by doping. The microstrain and dislocation density has increased significantly with elevated doping concentration as evidenced by increasing defects and strain reported earlier$^{40}$.
3.2. Raman Spectroscopy Study

Raman spectroscopy was employed to demonstrate the doping effect in MoS$_2$ NFs using a 532 nm excitation laser with the calibrated silicon Raman peak 521 cm$^{-1}$. The recorded Raman spectra of MoS$_2$ and Co-doped MoS$_2$ are shown in Figure 2. Furthermore, for the undoped MoS$_2$ nanoflakes, the Raman spectra display characteristic peaks at 281, 377, 404, and 454 cm$^{-1}$ arising from the E$_{1g}$, E$_{12g}$, A$_{1g}$ and longitudinal acoustic phonon mode (A$_{2u}$) of 2H-MoS$_2$.$^{51,52}$ The two intense peaks are located at $\sim$377 cm$^{-1}$ (E$_{12g}$ mode) corresponding to the in-plane vibration of S and Mo atoms and $\sim$404 cm$^{-1}$ (A$_{1g}$) attributing to the relative vibration of S atoms in the out of plane direction.$^{53,54}$ In addition to these 2H vibrational Raman modes, two other weak vibrational modes at 232 cm$^{-1}$ (J$_2$) and 335 cm$^{-1}$ (J$_3$) appear in the undoped one assigned to the 1T phase. By contrast, for the 8% Co-doped MoS$_2$ NFs, the intensity of J$_2$ and J$_3$ has increased significantly along with the presence of the J$_1$ phase attributed to the 1T-MoS$_2$ phase. In the 8% Co-doped MoS$_2$ NFs the suppression in the E$_{12g}$ and A$_{1g}$ peak intensity has been observed. This suggests that a high amount of cobalt doping enables phase transformation of the 2H- phase to 1T phase in the 8% Co-doped MoS$_2$ NFs. In the case of 8% Co-doped MoS$_2$ NFs, redshifts of the two peaks (E$_{12g}$ and A$_{1g}$) were detected from 377.72 cm$^{-1}$ to 374.78 cm$^{-1}$ and from 404.27 cm$^{-1}$ to 402.32 cm$^{-1}$, respectively. Specifically, the absence of sulfur atoms in few-layer MoS$_2$ would

![Figure 1. (a) XRD Pattern of various percentages of cobalt doped MoS$_2$ NFs. Rietveld refinement of (b) undoped, (c) 8% Co doped MoS$_2$.](image-url)
induce the redshifts of both the Raman peaks as reported by Kim et al.\textsuperscript{55} Tensile strain appearing in MoS\textsubscript{2}, directly related to the increase of the lattice parameters, redshifts both E\textsubscript{12g} and A\textsubscript{1g} peaks as observed by Yang et al.\textsuperscript{56} and Chaudhury et al.\textsuperscript{57} Thus, a possible explanation is that sulfur vacancies and tensile strain lead to bond softening and increased lattice parameters. Additionally, we found that the redshift of E\textsubscript{12g} mode contributed by the in-plane opposite vibration of two S atoms with respect to Mo atom is always larger than that of A\textsubscript{1g} mode caused by the out of-plane vibration of S atoms.\textsuperscript{58} The absence of sulfur atoms would have a larger effect on E\textsubscript{12g} mode due to the presence of in-plane chemical bonds between S and Mo atoms\textsuperscript{59} showing a gradual increase in Δk (difference in k) between E\textsubscript{12g} and A\textsubscript{1g} modes. Table 1 shows that there is a gradual increase of Δk between E\textsubscript{12g} and A\textsubscript{1g} in 8% of Co-doped MoS\textsubscript{2} NFs compared to the undoped ones. Additionally, chemical doping induced strain in the lattice changes the bond length and hence increase in Δk occurs. Observed increase in E\textsubscript{12g}/A\textsubscript{1g} intensity ratio and increased FWHM of A\textsubscript{1g} in 8% Co-doped MoS\textsubscript{2} compared to undoped one, is an indication of stacking of more number of layers along the in-plane direction and suppression of the out-plane movement related to the mode\textsuperscript{60}. The significant increase in FWHM and the downshift of A\textsubscript{1g} frequency as observed in the 8% Co-doped MoS\textsubscript{2} case supports the presence of zigzag edges forming structural disorder.\textsuperscript{61} The shifts and differences between the vibrational Raman E\textsubscript{12g} and A\textsubscript{1g} peaks with Co doping are represented in Table 1.

![Figure 2](image-url)

**Figure 2.** Different Raman modes showing presence of 1T and 2H phase in undoped and 8% Co doped MoS\textsubscript{2}
Table 1. Variation of Characteristic Raman modes of undoped and 8% Co doped MoS$_2$ NFs

<table>
<thead>
<tr>
<th>Co doping percentages</th>
<th>$E_{2g}^{1}$ (cm$^{-1}$)</th>
<th>$A_{1g}$ (cm$^{-1}$)</th>
<th>$\Delta k$ (cm$^{-1}$)</th>
<th>FWHM ratio ($A_{1g}$/$E_{2g}^{1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>377.72</td>
<td>404.27</td>
<td>26.55</td>
<td>0.82</td>
</tr>
<tr>
<td>8%</td>
<td>374.78</td>
<td>402.32</td>
<td>27.54</td>
<td>1.62</td>
</tr>
</tbody>
</table>

3.3. Morphology and Microstructure study

3.3.1. SEM image analysis

Figure 3 (a) and (b) show the FESEM images of the as-prepared 8% Co-doped MoS$_2$ nanoflakes indicating the formation of 3D hierarchical fluffy petaloid architecture. Each flower consists of several interconnected nanopetals in the form of nanoflakes. The average diameter of the undoped, 8% Co-doped MoS$_2$ flowers are about ~ 200 nm, ~1.5 μm, lateral dimensions are ~130 nm, ~240 nm and thickness lies within 10 nm. The lateral size of the MoS$_2$ NF increases with the incorporation of more Co dopants. The reason for the formation of larger nanoflowers with higher dopant content may be ascribed to the accumulation of dopant and defect-induced charge on the surface and edge of the lamellar structure contributing to the electrostatic attraction between them which can be validated by zeta potential measurement. Fig. 3 (c) and (d) show the EDAX elemental data analysis and plot indicating proper distribution and presence of Mo, S and Co in 8% Co-doped MoS$_2$ NFs. However theoretically calculated stoichiometric ratio of Co, Mo, S (0.03: 0.31: 0.66) for 8% Co-doped MoS$_2$ matches well with experimentally found value having slight variation (0.05: 0.41: 0.53) possibly due to the presence of S vacancies.
3.3.2. TEM image analysis

The detailed information about the microstructure of undoped and 8% Co-doped MoS\(_2\) NFs can be further unfolded by TEM image analysis. The thin interlaced flakes of MoS\(_2\) convert to a bigger nanostructure having sheet-like morphology with larger lateral dimensions which can be well understood in Fig. 4 (a) and (d). The inset of Fig. 4 (a) shows diffused rings in the SAED pattern of undoped MoS\(_2\) whereas the inset of Fig. 4 (d) shows distinct spots in SAED pattern diffraction planes indicating increased crystalline nature upon doping in 8% Co-doped MoS\(_2\). Figure 4 (b) clearly shows the magnified image of interlaced flakes of undoped MoS\(_2\) where interlayer distance is found to be ~0.62 nm forming a 14–16-layer system. In the case of 8% Co-doped MoS\(_2\), it has been observed that the number of layers lies within 4-8 layers having extended interlayer distance ~0.65 nm as shown in Fig. 4 (e) due to the appearance of doping-induced lattice strain.\(^{39}\)

Fig. 4 (c) shows the prominent presence of 2H and 1T phase and defects
in the vicinity of 1T phase. The presence of edge-terminated zigzag orientation in 8% Co-doped MoS$_2$ has been indicated by an arrow as shown in Fig. 4 (f). According to Tinico et al., such type of zigzag orientation in vertically oriented MoS$_2$ is responsible for metallic behaviour.$^{62}$

Figure 4. TEM images showing (a), (b) thin nanoflakes like morphology and interplanar spacing 0.62 nm of undoped MoS$_2$, (c) shows prominent presence of 2H, 1T phases, sulfur vacancies (V$_s$, encircled) present in 8% Co doped MoS$_2$ (d) interlaced flakes are summed up forming larger nanoflakes of 8% Co MoS$_2$; (e), (f) shows the extended interplanar spacing 0.65 nm and presence of zigzag edges in 8% Co doped MoS$_2$

3.4. XPS Study

The chemical composition and prominent presence of 1T phase along with the 2H phase in undoped$^{40}$ and 8% Co-doped MoS$_2$ have been verified by X-ray photoelectron spectroscopic (XPS) measurement. The typical B.E peaks of Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ peaks corresponding to the 2H phase of 8% Co-doped MoS$_2$ appear at 228.37, 231.75 eV, as shown in Fig. 5 (a). Two extra peaks corresponding to Mo 3d$_{5/2}$ and 3d$_{3/2}$ of 1T characteristic phase are shifted to $\sim$0.5-1 eV. Similarly, the binding energy peaks corresponding to S 2p$_{3/2}$ and S 2p$_{1/2}$ of the 2H phase appeared at 161.63, 162.79 eV in case of 8% Co-doped MoS$_2$, as shown in Figs. 5 (b). Two other extra peaks shifted about $\sim$ 0.5 eV from the S 2p$_{3/2}$ and S 2p$_{1/2}$ of the 2H phase are assigned
to the 1T phase. It has been observed that the doublets corresponding to Mo$^{4+}$ and S$^{2-}$ are shifted to lower binding energy with a gradual increase of Co dopant as observed in 8% Co-doped MoS$_2$ when compared with undoped one as shown in Fig 5 (a) and (b), affirming the loss of sulfur atoms in the sample. The difference between Mo 3d$_{3/2}$ and 3d$_{5/2}$ binding energy peaks corresponding to 1T phase is 3.1 eV confirming the emergence of Mo$^{5+}$ ions in 8% Co-doped MoS$_2$. By analyzing the XPS spectra, the S: Mo peak ratio for 4% Co-doped MoS$_2$ is 37% smaller than 2% Co-doped MoS$_2$ NFs. In addition, based on the analysis of the Mo 3d peak area, it is deduced that the content of Mo$^{5+}$ in MoS$_2$ NFs is around 26%, demonstrating a defect-rich structure. Four main peaks corresponding to Co 2p$_{3/2}$ at 780.34 eV (Co$^{3+}$), 785.27 eV (Co$^{2+}$) and Co 2p$_{1/2}$ at 791.33 eV (Co$^{3+}$), 798.07 eV (Co$^{2+}$) are found in 8% Co-doped MoS$_2$ as shown in Fig. 3 (c) similar to the report in case of Co species found in CoS$_2$. Also, another two peaks arising at 790.73 eV and 803.24 eV signifies the existence of satellite shake-up peaks. The binding energy peak of Co 2p$_{3/2}$ at 780.34 eV resembles the CoMo$_2$S$_4$ phase, affirming the uniform substitution of Mo atoms by Co$^{2+}$ along the {002} or the S-edge planes. The presence of the elements C, Mo, S, O and Co are revealed in the survey spectrum (wide scan) of undoped and 8% Co-doped MoS$_2$ as shown in Fig. 5 (d). The B.E. peaks corresponding to different oxidation states of Mo, S, and Co elements present in our samples are listed in Table 2.
Table 2. Position of binding energy peaks of Mo, S and Co elements corresponding to 1T and 2H phase of undoped and 8% Co-doped MoS$_2$

<table>
<thead>
<tr>
<th>Doping amount</th>
<th>1T Mo $3d_{5/2}$ (eV)</th>
<th>1T Mo $3d_{3/2}$ (eV)</th>
<th>2H Mo $3d_{5/2}$ (eV)</th>
<th>2H Mo $3d_{3/2}$ (eV)</th>
<th>1T S $2p_{3/2}$ (eV)</th>
<th>1T S $2p_{1/2}$ (eV)</th>
<th>2H S $2p_{3/2}$ (eV)</th>
<th>2H S $2p_{1/2}$ (eV)</th>
<th>Co $^{3+}$ Co $^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>228.25$^{40}$</td>
<td>231.12$^{40}$</td>
<td>229$^{40}$</td>
<td>231.5$^{40}$</td>
<td>161.7$^{40}$</td>
<td>162.0$^{40}$</td>
<td>162.96$^{40}$</td>
<td>163.37$^{40}$</td>
<td>-------</td>
</tr>
<tr>
<td>8%</td>
<td>227.88</td>
<td>231.25</td>
<td>228.37</td>
<td>231.75</td>
<td>161.17</td>
<td>162.31</td>
<td>161.63</td>
<td>162.79</td>
<td>780.34</td>
</tr>
</tbody>
</table>

3.5. Electronic Transport Property Study

Figure 6 shows the temperature-dependent resistivity curves for all undoped and Co-doped MoS$_2$, exhibiting typical semiconductor behaviour. The resistivity eventually decreases with an increase in doping concentration and it is clearly seen in low-temperature regimes. This supports the fact of the increase in carrier concentration with the incorporation of more proportions of 1T phase with Co doping$^{71}$. Thermal excitation of electrons from donor levels...
to the conduction band takes place with the increase in temperature. Temperature-dependent resistance can be written in an Arrhenius form:

\[ \sigma (T) = \sigma_0 \exp \left( -\frac{E_a}{k_B T} \right) \]

where \( \sigma \) is the conductivity, \( \sigma_0 \) is the pre-exponential factor, \( k_B \) is the Boltzmann constant, and \( E_a \) is the activation energy. Figures 6 (a) - (f) shows the plots of the conductivity in log scale as a function of 1000/T from 217 K to 250 K of the samples undoped and 2%, 4%, 6%, 8% Co-doped samples. As a boundary from 200 K, we obtained different thermal activation energy regions. The data are fitted to a line with different slopes at this temperature region. We obtained activation energy for undoped, 2%, 4%, 6% and 8% are 85.13 meV, 65.73 meV, 47.38 meV, 33.9 meV and 85.3 meV respectively (above 200 K). The activation energy is observed to be much lower than the band gap energy of MoS\(_2\) samples. Such low activation energy strongly suggests that native defects such as sulfur vacancies and impurities are present in the as-synthesized MoS\(_2\) samples which are already verified in the XPS result. The decrease of activation energy with an increase of doping concentration suggests that donor carrier density lifts the Fermi level position in the band gap which supports the result obtained from UV-Visible absorption spectra.\(^{40}\) It has been studied in a doped semiconductor that a major portion of the free electrons is recaptured by donor atoms themselves at low temperatures.\(^{72}\) The electrons suffer from lacking sufficient energy to jump from donor levels to the conduction band. At this stage, the electrons conduct through hopping from one level to another in the impurity band and free-electron band conduction becomes less significant.\(^{72}\) Thermal activations are due to deep donor level ions contributing to the conduction band. For higher cobalt doped MoS\(_2\) at temperature < 200 K, the activation energy \((E_a)\) drops and other transport mechanisms could interplay in addition to the nearest neighbour hopping. The weak temperature dependence of resistance at low temperatures can be explained by the mechanism of electron hopping through impurity levels formed near the conduction band edge of cobalt-
doped MoS$_2$. In addition to this, temperature cooling is accompanied by a rapid rise of the electrical resistivity as electrons hop from the conduction band to the localized impurity states. Therefore, the conduction mechanisms in these Co-doped MoS$_2$ samples can be explained by the combination of two types of conduction models such as variable range hopping (VRH), \( \sigma_{VRH} = \sigma_{0VRH} \exp \left[-\left(\frac{T_{0VRH}}{T}\right)^{1/4}\right] \) and thermal excitation by nearest neighbour hopping (NNH), \( \sigma_{th} = \sigma_{0th} \exp\left[\frac{(E_a/kT)}{1000/T}\right] \), where \( \sigma_{0VRH}, T_{0VRH}, \) and \( \sigma_{0th} \) are constants. The first one describes carrier hopping in localized states at a lower temperature range whereas the second one describes carriers that have been thermally excited from localized state to conduction band. The parameters were evaluated from the linear fitting method by plotting \( \ln\sigma\sim T^{-1/4} \) (VRH), and \( \ln\sigma\sim 1000/T \) (NNH) in different temperature regions to investigate the involved temperature-dependent transport processes. Those parameters are listed in Table-3. The resistivity rises at low temperature and passes the VRH test for 2%, 4%, 8% Co-doped samples (50 K- 70 K) and for 6% Co (50 K- 110 K) at a low-temperature range as shown in Figs. 7 (a), (b) (d) and (c), respectively. It suggests that the conduction in these pellet-formed powder samples is due to the thermally assisted tunneling of the charge carriers through the grain boundary barrier and transition from donor level to the conduction band. It is observed that at low temperature, the resistivity of 8% Co-doped MoS$_2$ is very less compared to undoped one due to incorporation of metallic 1T phase in 2H MoS$_2$ with the increase of cobalt doping concentration. Increasing the Co-doping concentration will reduce the resistance, and in Table 3 it has been observed that the activation energy decreases from 65.73 meV to 33.59 meV as the concentration of Co atoms increase from 2% to 6%. It has been observed that in case of heavy doping of Co ion (8% Co) in MoS$_2$ the activation energy is increased. This is attributed to the rise in atomic defects which are electrically active at the grain boundary.\textsuperscript{73}
Figure 6. Logarithmic plot of resistivity with temperature of (a) undoped and Co doped MoS$_2$. Linear variation of conductivity with inversion of temperature to test the (b) undoped (c) 2%, (d) 4%, (e) 6% and (f) 8% Co doped MoS$_2$ which satisfy the thermal excitation process of transport.
Table 3. Various transport mechanisms in different temperature regimes observed in cobalt doped MoS\(_2\)

<table>
<thead>
<tr>
<th>Samples</th>
<th>(\sigma_{\text{VRH}}) (Ωm(^{-1}))</th>
<th>(T_{\text{VRH}}) (K)</th>
<th>(\sigma_{\text{EVRH}}) (Ωm(^{-1}))</th>
<th>(T_{\text{EVRH}}) (K)</th>
<th>(\sigma_{\text{Th}}) (Ωm(^{-1}))</th>
<th>(E_A) (meV)</th>
<th>Adj.R(^2)</th>
<th>Temperature Coefficient of Resistance (TCR) (K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS(_2)</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>3.7397</td>
<td>85.13</td>
<td>0.9998</td>
<td>-3.74×10(^{-2})</td>
</tr>
<tr>
<td>2% Co</td>
<td>3.932×10(^9)</td>
<td>1.67×10(^8)</td>
<td>352.7</td>
<td>30043.28</td>
<td>0.2686</td>
<td>65.73</td>
<td>0.99825</td>
<td>-3.12×10(^{-2})</td>
</tr>
<tr>
<td>4% Co</td>
<td>5.92×10(^{11})</td>
<td>1.08×10(^7)</td>
<td>6.5023</td>
<td>9583.31</td>
<td>0.4832</td>
<td>47.37</td>
<td>0.99828</td>
<td>-1.85×10(^{-2})</td>
</tr>
<tr>
<td>6% Co</td>
<td>0.7780</td>
<td>2931986</td>
<td>7.5341</td>
<td>12500</td>
<td>0.1267</td>
<td>33.59</td>
<td>0.99871</td>
<td>-1.29×10(^{-2})</td>
</tr>
<tr>
<td>8% Co</td>
<td>5597.07</td>
<td>2.673×10(^7)</td>
<td>1.769</td>
<td>18770.31</td>
<td>0.00647</td>
<td>85.3</td>
<td>0.9997</td>
<td>-2.93×10(^{-2})</td>
</tr>
</tbody>
</table>

Figure 7. Temperature dependent conductivity plot of 2%, 4%, 6% and 8% Co doped MoS\(_2\) (a), (b), (c), (d) \(\ln\sigma - T^{1/4}\) plot of 2%, 4%, 6% and 8% Co doped MoS\(_2\) to test the VRH mechanism.
3.6. EPR Analysis

The room temperature electron paramagnetic resonance spectra (EPR) of various percentages of cobalt doped MoS$_2$ nanostructures are shown in Fig. 8. The undoped MoS$_2$ shows a prominent resonant peak of low intensity at the magnetic field of 3446 G with the $g = 2.0005$. This signal may come from the unpaired electrons caused by unsaturated coordination structures e.g., vacancies, defects such as S vacancies, acting as paramagnetic centers. The EPR signal in the higher magnetic field is indicated using an arrow in Fig. 8 at $g = 1.89$ very close to $g$ values of oxygenated species for Mo$_5^{5+}$ in amorphous or unsupported sulfides. The maximum EPR signal has been observed in 2% Co-doped MoS$_2$ NFs and decreases gradually with an increase in Co dopant amount. The expression

$$g = hν/βH_0$$

is used to calculate the electron g factors, where $ν = 9.65$ GHz (frequency), $h = 4.135 \times 10^{-15}$ eV.s (Planck constant), $β = 5.788 \times 10^{-5}$ eV T$^{-1}$ (Bohr magnetron) and $H_0$ is the resonance magnetic field. Co doping with different concentrations in MoS$_2$ does not induce any new peak or change in the EPR spectra. However, a peak shift towards the lower magnetic field has been observed in all the doped MoS$_2$ samples. In Fig. 8, the prominent resonance peaks are witnessed at the magnetic field of 3435 G ($g = 2.007$), 3433 G ($g = 2.008$), 3439 G ($g = 2.005$), 3443 G ($g = 2.002$) for 2 at% Co, 4 at% Co, 6 at% Co and 8 at% Co-doped MoS$_2$ samples, respectively, which attributes to the enhanced ferromagnetic coupling with the increase in Co concentration. Eventually, the g value reaches a maximum of 4 at% Co-doped MoS$_2$. The 1T regions tend to produce more Mo$_{4+}$ spins by expanding in the less dense S vacancy regions. However, in the case of higher cobalt concentration (8 at%), the proportion of the 1T phase is added up to 48%. In this case, S atoms are surrounded by a majority of the Mo atoms compared to S vacancies whereas few of them existed as isolated Mo$_{4+}$ spins. This explains the origin of the
ferromagnetic coupling with S atoms, resulting in a rise of ferromagnetism in MoS$_2$ nanoflakes macroscopically.$^{31}$

![EPR spectra of various percentages of cobalt doped MoS$_2$ NFs.](image)

**Figure 8.** EPR spectra of various percentages of cobalt doped MoS$_2$ NFs.

### 3.7. VSM data analysis

The magnetic property (M-T and M-H at 10 K, 100 K and 300K) of undoped, 2% Co, 6% Co and the highest Co (8% at. wt) doped MoS$_2$ samples were studied through VSM as shown in Fig. 9. Both the undoped and 2% Co-doped MoS$_2$ samples show paramagnetic behaviour originating from free electrons contributed from defects and a small proportion of 1T phase whereas 2% Co-doped MoS$_2$ show higher magnetic moment compared to the undoped one as shown in the inset Fig. 9 (a). As reported by Nair *et al.* existence of point defects such as vacancies and the introduction of fluorine adatoms in graphene induces notable paramagnetism.$^{75}$ However, a paramagnetic to ferromagnetic transition has been distinctly found above 2% Co doping. The ZFC- FC feature in the M –T curve of 8% Co-doped MoS$_2$ NFs, as shown in Fig. 9 (b), almost retraces the same path indicating intrinsic single-phase ferromagnetism. The highest saturation magnetization ($M_s$) at 10 K is 0.42 emu/g and 1.2 emu/g, remanence magnetization ($M_r$) is 0.06 emu/g and 0.045 emu/g and coercivity are ~150 Oe, 70 Oe corresponding to 6% Co and 8% Co-doped MoS$_2$ nanoflakes respectively as shown
in Figure S2 (c) and Fig. 9 (d). Since our undoped MoS$_2$ possesses feeble paramagnetic nature, it is fair to assume that the robust magnetism in 6% Co, 8% Co-doped MoS$_2$ arises as a consequence of doping. The magnetism in multilayer MoS$_2$ and its doped analogues depends on the presence of zigzag edges, type of defects, vacancies, lattice strain, and the dopant concentration. Theoretical calculations by Wang et al.$^{76}$ revealed that low concentrations of 4% and 6% of Co doping in the Mo vacant sites of the basal planes result in stable magnetic moments at room temperature. Yun et al.$^{77}$ and Saab et al.$^{78}$ also reported tuning of electronic and magnetic properties due to doping of metal ions in the MoS$_2$ lattice. The high $M_S$ observed in Co-doped MoS$_2$ suggests that the robust ferromagnetism here originates not from the strain in the layer but rather from the ferromagnetically favourable ordering of Co$^{2+}$ ions.$^{50}$ The effective Bohr magneton number for ($p_{\text{eff}}(\text{Co})$) and the value of Curie constant (C) were calculated using the following formula

$$
(p_{\text{eff}}(\text{Co}))^2 = x g^2 S_{(\text{Co}^{2+})} (S_{(\text{Co}^{2+})} + 1) + (1-x) g^2 S_{(\text{Co}^{3+})} (S_{(\text{Co}^{3+})} + 1) \quad \text{(1)}
$$

$$
(p_{\text{eff}}(\text{Co}))^2 = 3Ck/N\mu_B^2 \quad \text{(2)}
$$

and where $g=2$ stands for the Lande’ $g$-factor of the cobalt ions, and $S_{(\text{Co}^{2+})}$, $S_{(\text{Co}^{3+})}$ stand for the total spin quantum numbers for Co$^{2+}$ and Co$^{3+}$ ions respectively, $k$ is the Boltzmann constant, $N$ is the Avogadro number and $\mu_B$ stands for the Bohr magneton. The value of $p_{\text{eff}}(\text{Co})$ obtained in various amounts of Co-doped MoS$_2$ NFs lies in between the theoretical value of $p_{\text{eff}}(\text{Co}^{2+}) = 3.87$ and $p_{\text{eff}}(\text{Co}^{3+}) = 4.89$ due to the presence of the mixed-valence state of Co in Co-doped MoS$_2$ NFs. Again, the value of Curie temperature of 6%, 8% Co-doped MoS$_2$ NFs was obtained from minima of $dm/dT$ vs. $T$ plot. The magnitude of the Curie constant (C) for 6% and 8% Co-doped MoS$_2$ nanoflakes were calculated using equation (2) by putting the value of $p_{\text{eff}}(\text{Co})$. The variation of saturation magnetization ($M_s$), Curie temperature ($T_c$), Curie constant (C), $p_{\text{eff}}(\text{Co})$ and the percentage amount of Co$^{2+}$/Co$^{3+}$ ions present in various amounts of Co-doped MoS$_2$ NFs are enlisted in Table 4.
To study the origin and variation of the observed ferromagnetism in MoS$_2$ NFs with Co doping, it is necessary to point out the role of the 1T phase and cobalt ion incorporation in the 2H MoS$_2$ matrix. The fact that Co dopant atoms can effectively introduce ferromagnetism in MoS$_2$ nanoflakes and it has been confirmed by the magnetic measurement results. Herein, we only consider the magnetic moment introduced in the MoS$_2$ NFs through the substitution of Mo atoms by Co atoms. According to crystal field theory 4d and 3d orbitals corresponding to Co$^{2+}$/Co$^{3+}$ remain in different degenerate states in 2H and 1T coordination. The Mo$^{4+}$ ion corresponding to 2H coordination split into three energy levels: $(d_{z^2})$, $(d_{x^2-y^2}, d_{xy})$, $(d_{xz}, d_{yz})$ while the 1T has two levels: $(d_{xz}, d_{yz})$ and $(d_{x^2-y^2}, d_{z^2})$ as shown in Fig 10 (a). As described in Fig. 10 (a), two 4d electrons occupy the $d_{z^2}$ orbital of Mo$^{4+}$ ion spin-antiparallel, thus giving net zero magnetic moments in the 2H phase. In the case of the 1T phase of the MoS$_2$, the lower

**Figure 9.** (a) M vs T plot of undoped, 2%, 6%, 8% Co doped MoS$_2$ at an applied field 500 Oe; inset is showing undoped and 2% Co doped M-T curve, (b) individual ZFC- FC curve of 8% Co doped MoS$_2$ indicating $T_c$~139 K, (c) $\delta m/\delta T$ plot of 8% Co doped MoS$_2$ showing $T_c$~139 K. (d) $1/\chi$ vs T with linear fitting having ($T_c$~139 K) of 8% Co doped MoS$_2$; inset shows magnified image of M vs H hysteresis loop of 8% Co doped MoS$_2$ at 10 K having 70 Oe coercive field; (e) Hysteresis loop at 10 K, 50 K, 100 K, and 300 K; (f) M-H loop of 8% Co doped MoS$_2$ showing room-temperature ferromagnetism at 300 K in magnified scale.
energy levels (d_{xz}, d_{yz}, d_{xy}) are occupied by the two 4d electrons spin-parallelly contributing net
magnet moments in the 1 T phase of Mo atoms.\textsuperscript{79} Therefore, it can be assumed that the presence
of ferromagnetism is directly connected to the proportion of both 1 T and 2H phases in MoS\textsubscript{2}
nanoflakes. Seven and six 3d electrons are corresponding to the Co\textsuperscript{2+} and Co\textsuperscript{3+} configuration
contributing three and four unpaired electrons in the octahedral geometry of the Co\textsuperscript{2+} and Co\textsuperscript{3+}
configuration, respectively. The observed magnetic moment varies monotonically with
proportions of 1T phase present in the sample. In undoped MoS\textsubscript{2}, the proportion of 1T phase
was 18\% having the lowest magnetic moment as shown in EPR analysis. The proportion of 1T
concentration increases gradually with the incorporation of cobalt dopant. The proportion of
1T phase in undoped, 2\%, 4\%, 6\% and 8\% Co-doped MoS\textsubscript{2} samples are found to be 18\%, 26\%,
39\%, 42\%, 48\%, respectively. The magnetic moment value rises as 1T phase concentration
increases with an increase in Co–dopant as obtained from experimental results.

To further explain the origin of ferromagnetism in Co-doped MoS\textsubscript{2} systems, the bound
magnetic polarons (BMPs) model is utilized.\textsuperscript{80–82} The two main results are obtained from the
XPS spectra: i) S vacancies are typical defects in hydrothermally synthesized MoS\textsubscript{2} nanoflakes
and ii) the substituted Co atoms can contribute two holes. Thus the Co\textsuperscript{2+} dopants provide the
local magnetic moments in addition to the carriers needed to couple these moments.\textsuperscript{80} Under
this condition, the electron distribution changes causing a strong interaction among the spin
impurities. Unintentional sulfur vacancies are formed in MoS\textsubscript{2} nanoflakes during the
hydrothermal synthesis process. As a result, BMPs could be exhibited with localized holes and
the S vacancies surrounded by a large number of Mo\textsuperscript{4+} spins.\textsuperscript{80} The Mo\textsuperscript{4+} spins and S vacancy
spin are aligned in parallel, leading to the formation of a BMP. Cai \textit{et al.} observed that the 2H-
1T transformation always occurs near the defects.\textsuperscript{52} Such ferromagnetism appears due to the
overlapping of BMPs and their ferromagnetic coupling to each other as shown in Fig. 10 (b).
Additionally, with the Mo$^{4+}$ ions, the doped Co ions can be bounded by the S vacancies as shown in Fig. 10 (b). Only those Co ions arranged at suitable distances can interact ferromagnetically possibly through some indirect coupling mechanism. In this manner, numerous BMPs can be created by the Co ions in the vicinity of the S vacancies. They are ordered ferromagnetically and establish long-range room-temperature ferromagnetism in the Co-doped MoS$_2$ nanoflakes.

![Figure 10](image)

**Figure 10.** (a) Electron orbital degenerate states of Mo atoms (Mo$^{4+}$ ionic state) in 1T and 2H configuration and Co atoms (Co$^{2+}$, Co$^{3+}$ ionic state). (b) Schematic representation of bound magnetic polaron model mediated by vacancy and Co dopant in MoS$_2$ NFs. 1T phases are induced around vacancy and Co atom forming spin polarized states.

**Table 4.** Variation of magnetic parameters with various amounts of Co doping (0%, 2%, 6%, 8%) in Co-doped MoS$_2$ NFs

<table>
<thead>
<tr>
<th>Doping percentage</th>
<th>$M_s$ (emu/g)</th>
<th>$T_c$ (K)</th>
<th>C (emu K Oe$^{-1}$ mol$^{-1}$)</th>
<th>$P_{eff}(\text{Co}^{2+}, \text{Co}^{3+})$ (calculated)</th>
<th>Variation of Co$^{2+}$/Co$^{3+}$ ions in percentage with Co doping</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\text{Co}^{2+}$</td>
</tr>
<tr>
<td>0%</td>
<td>****</td>
<td>****</td>
<td>****</td>
<td>****</td>
<td>65</td>
</tr>
<tr>
<td>2%</td>
<td>****</td>
<td>****</td>
<td>2.24</td>
<td>4.26</td>
<td>65</td>
</tr>
<tr>
<td>6%</td>
<td>0.42</td>
<td>131</td>
<td>2.32</td>
<td>4.32</td>
<td>59</td>
</tr>
<tr>
<td>8%</td>
<td>1.2</td>
<td>139</td>
<td>2.45</td>
<td>4.37</td>
<td>54</td>
</tr>
</tbody>
</table>
To simulate 2%, 6% and 8% Co doping in MoS$_2$, 5×5×1, 3×3×1 and 3×2×1 bulk MoS$_2$ supercells were created respectively and then one Mo atom from the supercell was substituted with one Co atom, to incorporate the desired doping level, as shown in Fig. 11 (a), (b). The average Mo-Mo, Mo-S bond length obtained theoretically from our calculation agrees well with the experimental value$^{85}$ in the case of undoped and doped cases. In all the doped cases small variation of average Co-Mo bond length values and the average Mo-Mo bond length around the dopant site is observed from the Mo-Mo bond length value in the undoped cases. This suggests that the substitutional doping of Co at Mo does not change the symmetry around the dopant site. All the calculations are performed on the semiconducting 2H phase, since this phase is seen to be the dominant one over the metallic 1T phase, in all the cases.

The total and projected density of states (TDOS and PDOS) of undoped MoS$_2$, 2%, 6%, 8% Co-doped MoS$_2$ are displayed in Fig. S3 (a)-(d) and Fig. 11 (a)-(d), respectively. The symmetry of the up spin and down spin DOS throughout the energy range, as shown in Fig. 11 (a), validates the nonmagnetic nature of the undoped MoS$_2$ NFs. In the case of doped systems, it is seen that the doping of the Co atom in one layer does not affect the other layer. The reason might be the weak interlayer interaction and the large interlayer separation. The isolated Co atom possesses an electronic configuration of $3d^74s^2$ having three additional valence electrons compared to the Mo atom, and it contributes to the magnetic moment in the Co-doped system.

The overall magnetic moment of the supercell with one Co atom substituting one Mo atom and the local magnetic moment of the constituent atoms for 2%, 6%, 8% Co-doped MoS$_2$ NFs have been represented in Table 5. The Co atom induces spin polarization on the neighbouring 6 Mo atoms and S atoms. The spins of the six neighbouring Mo atoms are coupled to the Co atom with an average moment of 0.2 $\mu_B$ in the 6% Co-doped case. An average magnetic moment of 0.04 $\mu_B$ is contributed by spin-polarized p orbitals of the S atoms. More obviously, the Co
dopant site remains in trigonal prismatic symmetry even after structural relaxation. As shown in Fig. 11 (c) to (f), with the doping of the Co atom replacing a Mo atom, a distinct spin splitting appears near the Fermi level contributing to large ferromagnetism. This is attributed to the defect states associated with the doped Co atom, $p$ states of the adjacent S atoms, and $d$ states of the nearby Mo atoms, albeit mainly Co-d and Mo-d states. Due to the overlapping among the Co-d, Mo-d, and S-p orbitals the band edge structures change significantly in comparison with undoped MoS$_2$. For the C$_{3v}$ symmetry around the dopant site, the doping produces five 3d states within the band gap which split into three sub-levels $e_1$, $e_2$, and $a$, among them one mono- and two doubly-degenerate. The Co $e_1 (d_{xy}, d_{x^2-y^2})$ orbitals and $e_2 (d_{xz}, d_{yz})$ orbitals are strongly hybridized with S 3p orbitals and remain at relatively low energy levels in the spin-up channel, whereas in the spin-down channel they possess higher energy. The 3 extra non-bonding valence electrons occupy the lowest energy mono-degenerate $a (d_{z^2})$ and the first doubly-degenerate $d_{xy}, d_{x^2-y^2}$ states in the up spin channel. The down spin channel remains vacant at the Fermi level, at least in the low doping regime. The results obtained from the calculation, indicate an obvious asymmetry of the DOS around the Fermi level of the cobalt doped MoS$_2$, and it confirms that the substitution of Co at the Mo site gives rise to the spin-polarized state. Interestingly, the DOS indicates that Co-doped MoS$_2$ exhibits half-metallic behaviour in the 2% doping case, i.e., the DOS shows no gap in the spin-up channel and a semiconducting band gap in the spin-down channel which means being a semiconductor in one spin channel and metal in another. It is obvious from the calculation that, the asymmetry around the Fermi level has increased significantly with the increase in Co dopant concentrations, resulting in a net increase of total magnetic moment. Experimentally it has been demonstrated that Co doping up to a certain percentage can enhance ferromagnetism very well. The theoretical calculation for the Co doping in dominant phase 2H supercell of MoS$_2$ shows increasing behaviour of magnetic moment with an increase in doping concentration which supports the experimental
evidence obtained from VSM measurements. This is probably because the small contribution of the 1T phase has been neglected in the calculation since the 2H phase has always been the dominant one over the 1T phase. However, the calculation presents a clear picture of the environment around the dopant site, the local and global magnetism and the induction of magnetism from the dopant to the nearby Mo and S atoms. To visualize the nature of the impurity state initiated by the S defect, Salehi et al.\textsuperscript{88} discussed the influence of chalcogen defect on the electronic structure of the monolayer MoS\textsubscript{2} by assuming a single sulphur vacancy per supercell. Evidently, at high defect concentration, a midgap band is introduced by the sulphur vacancies nearby to the VBM having a bandwidth $\sim$ of 0.6 eV. Such types of defect states tend to become more delocalized due to the interaction between S vacancies. Additionally, a flat band appears just below the MoS\textsubscript{2} CBM which does not change notably with the concentration changes. The Mo 4d orbitals around the vacancies play the main role in the creation of midgap states, while the S 3p and 3d orbitals do not contribute considerably to the defect states of the gap region. The presence of sulphur vacancy shifts the Fermi level to the bottom of the conduction band due to the unsaturated electrons in the Mo orbitals around the vacancy defect. In the case of multi-layered MoS\textsubscript{2}, the effect of layers and their interactions come into the picture. In the case of multi-layered MoS\textsubscript{2} with S vacancy in each layer, an increase in the electron density of the unremoved S atoms has been observed which increases the repulsion of electrons between layers, increasing the interlayer distance as reported by Zhu et al.\textsuperscript{89} Additionally, a direct band gap with $\Gamma \rightarrow \Gamma$ transition is observed in addition to decrease in the band gap by introducing mid-gap defect in the forbidden region for the MoS\textsubscript{2} structures with S vacancies. This is quite different from the $\Gamma \rightarrow K$ transition as observed in bulk MoS\textsubscript{2} without defects. In the MoS\textsubscript{2} structures with S vacancies, the VBM is mainly composed of 4d orbital of Mo atom at $\Gamma$ point, while the doping band minimum is almost composed of 4d orbital of Mo atom and 3p orbital of S atom at $\Gamma$ point. This can be considered to be responsible for
such direct nature of $\Gamma \rightarrow \Gamma$ transition. Such type of defect and 1T phase enriched Co-doped half-metallic MoS$_2$ possessing robust ferromagnetism may possess greater potential in the application of spintronic and detection-based devices.

**Table 5.** Local magnetic moments of the dopant Co, the six neighbouring Mo and total magnetic moments in various percentages of Co-doped MoS$_2$ multi-layered systems

<table>
<thead>
<tr>
<th>Doping percentage</th>
<th>Local magnetic moments ($\mu_B$)</th>
<th>Total magnetic moments (μB)</th>
<th>(emu/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo Co</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>0 --</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2%</td>
<td>0.24 0.91</td>
<td>2.96 4.16</td>
<td></td>
</tr>
<tr>
<td>6%</td>
<td>0.20 1.10</td>
<td>2.94 5.77</td>
<td></td>
</tr>
<tr>
<td>8%</td>
<td>0.14 1.34</td>
<td>2.63 7.76</td>
<td></td>
</tr>
</tbody>
</table>
Figure 11. The atomic structure of (a) undoped MoS$_2$ supercell, (b) $3\times3\times1$ supercell of 6% Co doped MoS$_2$ from top view with a Co atom substituting Mo site. The big purple balls stand for the Mo atoms small yellow balls are sulphur atoms and blue balls are cobalt atom. The projected density of states (PDOS) corresponding to Mo $d$, S $p$ and Co $d$ states of (c) undoped MoS$_2$ supercell; (d) the supercell with 2% Co dopant; (e) the supercell with 6% Co and (f) the supercell with 8% Co dopant atom (the vertical dashed line indicates the Fermi level).
3.9. Electrochemical measurement

To unravel the effect of Co-doping on MoS$_2$ NFs the electrochemical performance of undoped MoS$_2$, 2% Co, 4% Co and 8% Co-doped MoS$_2$ as electrode materials are characterized by cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) measurements. The measurement is performed with three-electrode equipment, which consists of Ag/AgCl as a reference, Pt as the counter electrodes and one glassy carbon electrode loaded with a sample on it as the working electrode. Prepared working electrode is analysed by different scan rates (10–100 mV/s) within a potential window of -0.6 V to 0.2 V (undoped, 2% Co-doped), 0 V to 0.6 V (4% Co) and -0.8 V to 0.6 V (8% Co-doped MoS$_2$) using 1 M Na$_2$SO$_4$ electrolyte. The comparative CV representation of undoped, 2% Co, 4% Co and 8% Co-doped MoS$_2$ at a scan rate of 10 mV/s is represented in Fig. 12 (a). It has been observed from Fig. 12 (a) that 8% Co-doped MoS$_2$ shows the highest CV area at 10 mV/s scan rate which indicates better electrochemical performances compared to other MoS$_2$ moieties. Therefore, the CV plots of 8% Co-doped MoS$_2$ at different scan rates (10, 20, 40, 60, 80, 100 mv/s) are depicted in Fig. 12 (b). The variation of specific capacitances (calculated from CV profile) at different scan rates of undoped, 2% Co, 4% Co and 8% Co-doped MoS$_2$ are depicted in Fig. 12 (c) and their numerical values are enlisted in Table S1. The greater capacitive behaviour of 8% Co-doped MoS$_2$ is attributed to the following points: (1) the presence of a more metallic 1T phase resulting in high electrical conductivity and low internal resistance (2) 1T phase being more electrochemically active in the edge planes, (3) increased defects levels, validated from XPS and steady-state UV Vis. absorption spectra and BET surface area (for undoped and 8% Co-doped MoS$_2$ the BET surface area is 33.84 m$^2$/g and 43.47 m$^2$/g respectively) facilitated the charge transport and adsorption of transported ions within 8% Co-doped MoS$_2$ leading to rapid redox reactions. The area under the CV curve shows a symmetric rectangular-like shape revealing the better choice for energy storage.
application as an ideal supercapacitor. The specific capacitance of the symmetrical supercapacitor was calculated from the CV profile following equation (3)

\[ C_{sp} = \frac{\int I(V) \, dV}{vm\Delta V} \]  

where \( \int I(V) \, dV \) is the area under the CV curve, \( m \) is the mass of the electrode materials, \( v \) is the scan rate, and \( \Delta V \) is the potential window taken. The specific capacitance of 8% Co-doped MoS\(_2\) shows the highest specific capacitance of 217.9 F/g at a voltage scan rate of 10 mV/sec which is approximately 1.7, 1.5 and 1.3 times greater than undoped (98.1 F/g), 2% Co, 4% Co-MoS\(_2\) electrode (123.7 F/g) material, respectively. It has been observed that upon increasing the scan rate, the capacitive value decreases. Usually, at a higher scan rate, sufficient ion diffusion cannot take place within a constant time, and therefore, reflects a reduction of capacitance values. Similarly, the galvanostatic charge-discharge (GCD) technique was carried out to further evaluate the capacitance behaviour of as-synthesized materials at different current densities (Fig. 12 (d), Fig. S4 (b), Fig. S4 (d), Fig. S4 (f)). The GCD curve of 8% Co-doped MoS\(_2\) shows the symmetric charging and discharging curve which reveals the good capacitive behaviour of the 8% Co-doped sample. The specific capacitance of the hybrid material was derived from the GCD curve following equation (4)

\[ C_{sp} = \frac{I \times \Delta t}{m \Delta V} \]  

where \( I \) is the current (mA), \( \Delta t \) is the discharge time (s), \( m \) is active electrode materials (mg) and \( \Delta V \) is the potential window (V). The specific capacitance values of undoped, 2% Co, 4% Co, and 8% Co doped MoS\(_2\) electrodes with varying current densities obtained from the GCD plot have been enlisted in Table S2. It has been observed that specific capacitance values obtained from CV and GCD measurement are nearly same which indicates validation of our measurements and stability of the as-prepared electrode materials. To better understand the reason for the improved electrochemical performance of 8% Co-doped MoS\(_2\), electrochemical impedance spectroscopy (EIS) of undoped, 2% Co, 4% Co and 8% Co-doped MoS\(_2\) in the
frequency range of 1 Hz–100 kHz is performed (Fig. 12 (e)). The prepared MoS$_2$ nanostructures show the supercapacitor feature, i.e., a semicircle at higher frequencies, which is related to the surface area and electrical conductivity and a straight line at the lower frequency region. The intercept on the real axis is ascribed to the equivalent series resistance ($R_s$), and the diameter of the semicircle corresponds to the charge transfer resistance ($R_{ct}$) in the electrode/electrolyte system. The $R_s$ values for undoped, 2% Co, 4% Co and 8% Co-doped MoS$_2$ are 31.1 $\Omega$, 24.8 $\Omega$, 8.7 $\Omega$ and 18.9 $\Omega$, respectively. With the increase in cobalt doping the $R_s$ value decreases from low-doping (2% Co) to high-doping concentration (8% Co-doped MoS$_2$) which confirms that Co doping has enhanced the electrical conductivity of MoS$_2$ NFs. The 8% Co-doped MoS$_2$ electrode exhibits the smallest semicircle, indicating that the electrode has lower charge transfer resistance than the other two electrodes because the existing 1T phase and more available active sites decrease the charge transfer resistance. The 8% Co-doped MoS$_2$ show nearly vertical shapes because electrons could transfer fast as rapid ion diffusion occurs due to less resistance at the electrode-electrolyte interface. The low-frequency straight line shows the capacitive behaviour of MoS$_2$ nanomaterials (Fig. 12 (e)). The highest slope of the straight line parallel to the imaginary axis is obtained for 8% Co-doped MoS$_2$, suggesting that 8% Co-doped MoS$_2$ has optimal performance among the prepared MoS$_2$ nanostructures. Table 6 represents the comparative electrochemical performance of MoS$_2$, (pure or in composite form when used as a single electrode material) as published in previous works, with the results obtained from our highest Co-doped (8% Co) MoS$_2$ NFs indicating improved electrochemical behaviour of our material. Therefore, the doping-induced phase and defect engineering of the MoS$_2$ NFs for enhanced electrochemical property in supercapacitors paves the way toward the production of more efficient electrode materials by designing Co-doped 1T phase and defect-rich MoS$_2$ ultrathin NFs-based composites.
Figure 12. (a) Comparative CV curves of undoped, 2% Co, 4% Co and 8% Co doped MoS$_2$ NFs, (b) CV scans of 8% Co doped MoS$_2$ at different scan rates, (c) plot of specific capacitance at different scan rates for undoped, 2% Co, 4% Co and 8% Co doped MoS$_2$, (d) GCD plot of 8% Co-doped MoS$_2$ at different current densities, (e) Nyquist plots of undoped, 2% Co, 4% Co and 8% Co doped MoS$_2$ electrodes.
<table>
<thead>
<tr>
<th>Nanostructured electrode material</th>
<th>Electrolyte</th>
<th>Specific capacitance (Single electrode)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$ Nanosheets</td>
<td>1 M KCl</td>
<td>148 F/ g at 1 A/ g</td>
<td>[94]</td>
</tr>
<tr>
<td>MoS$_2$/PEI-GO</td>
<td>2 M Na$_2$SO$_4$</td>
<td>153.9 F/ g at 1 A/g</td>
<td>[95]</td>
</tr>
<tr>
<td>MoS$_2$/Graphene</td>
<td>1M Na$_2$SO$_4$</td>
<td>270 F/ g at 0.1 A/g</td>
<td>[96]</td>
</tr>
<tr>
<td>MoS$_2$/Graphene</td>
<td>6 M KOH</td>
<td>258 F/g at 2 A/g</td>
<td>[97]</td>
</tr>
<tr>
<td>MoS$_2$/a-C</td>
<td>6 M NaOH</td>
<td>163.7 F/ g at 0.5A/ g</td>
<td>[98]</td>
</tr>
<tr>
<td>MoS$_2$/CNT</td>
<td>1 M Na$_2$SO$_4$</td>
<td>74.05 F/g at 2 A/g</td>
<td>[99]</td>
</tr>
<tr>
<td>Carbon-MoS$_2$ yolk–shell microspheres</td>
<td>1 M Na$_2$SO$_4$</td>
<td>122.6 F/ g at 1A/g</td>
<td>[100]</td>
</tr>
<tr>
<td>8% Co doped MoS$_2$</td>
<td>1 M Na$_2$SO$_4$</td>
<td>201.4 F/ g at 1.5 A/g</td>
<td><strong>This work</strong></td>
</tr>
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</table>
4. Conclusion

The well-matched 1T phase incorporation in 2H- phase MoS$_2$ NFs using Co as a dopant in different wt. percentages (0%, 2%, 4%, 6%, 8%) has been successfully constructed via facile one-step hydrothermal technique. The evolution of the 1T phase, defects, vacancies and introduction of zigzag edges with Co doping has been verified using Raman, TEM and XPS measurement techniques. The robust ferromagnetism with Co doping has originated from ferromagnetic exchange interaction between Mo$^{4+}$ and Co$^{2+}$ with sulfur vacancy via the BMP model and magnetic moment contributed from zigzag edges. An asymmetry nature of the DOS and spin splitting near the Fermi level of Co-doped MoS$_2$ NFs contributed by d states of Mo and Co atoms and p states of neighbouring S atoms, confirms that substitutional doping of Co atom at the Mo site can effectively induce a spin-polarized state corresponding to ferromagnetism. The prominent feature of half-metallicity and formation of defect level within the MoS$_2$ band gap has been evidenced in DOS results. In addition, various type of transport mechanisms existing in different temperature regime has been explained and fitted well in the temperature variation resistivity curves. Moreover, Co-doping in MoS$_2$ shows better electrochemical performances due to the presence of more electrochemically active metallic 1T sites, edge defects, increased BET surface area and enhanced interlayer separation due to intercalated Co$^{2+}$/Co$^{3+}$ ions. This work demonstrates that Co-doped ferromagnetic 1T-MoS$_2$ NFs provide enlightenment for constructing Co-doped 1T-MoS$_2$-based heterojunctions for their promising application in spintronic and detection-based devices as well as in energy storage applications in the future.
Conflicts of interest

The authors declare no conflict of interest.

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