Intrinsic Ferromagnetism in Mn-Substituted MoS$_2$ Nanosheets Achieved by Supercritical Hydrothermal Reaction

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Doping atomically thick nanosheets is a great challenge due to the self-purification effect that drives the precipitation of dopants. Here, a breakthrough is made to dope Mn atoms substitutionally into MoS$_2$ nanosheets in a sulfur-rich supercritical hydrothermal reaction environment, where the formation energy of Mn substituting for Mo sites in MoS$_2$ is significantly reduced to overcome the self-purification effect. The substitutional Mn doping is convincingly evidenced by high-angle annular dark-field scanning transmission electron microscopy and X-ray absorption fine spectroscopy characterizations. The Mn-doped MoS$_2$ nanosheets show robust intrinsic ferromagnetic response with a saturation magnetic moment of 0.05 $\mu_B$ Mn$^{-1}$ at room temperature. The intrinsic ferromagnetism is further confirmed by the reversibility of the magnetic behavior during the cycle of incorporating/removing Li codopants, showing the critical role of Mn 3d electronic states in mediating the magnetic interactions in MoS$_2$ nanosheets.

2D nanomaterials such as the well-known graphene, hexagonal boron nitride, and transition metal dichalcogenides nanosheets have been a very active subject of research in the past decade.$^{[1]}$ Among them, MoS$_2$ nanosheets is one of the most studied 2D materials due to their fascinating properties including medium intrinsic band gap,$^{[2]}$ highly tunable charge-carrier type and concentration,$^{[3]}$ high on/off ratio,$^{[4]}$ and novel valley polarization properties.$^{[5]}$ These properties make MoS$_2$ nanosheets ideal material as fundamental building blocks in field-effect transistor, digital circuits,$^{[6]}$ and so on. Besides, MoS$_2$ nanosheets is a very promising material for the next-generation spintronics field,$^{[7]}$ primarily because of their long spin lifetime and suppressed spin relaxation.$^{[8]}$ However, at present the use of MoS$_2$ in spintronics field is prohibited by the inherently nonmagnetic nature of normal MoS$_2$ nanosheets. In a real spintronics device, the manipulations of spin orientations and transportations of carriers are commonly realized through switching the performance of magnetic semiconductors by external fields. Hence, how to render the MoS$_2$ nanosheets with robust ferromagnetism is an important issue for expanding the applications of MoS$_2$ nanosheets in spintronics.

Recently, tremendous efforts have been attempted and significant progresses have been made to activate the
ferromagnetism of the MoS\textsubscript{2} system.\textsuperscript{[7b,9]} One example is the work by Han et al.,\textsuperscript{[9d]} who induced weak ferromagnetism in pristine MoS\textsubscript{2} by using proton irradiation to generate sulfur vacancies. Strain-induced magnetism in single-layer MoS\textsubscript{2} with S and Mo vacancies is also reported by Tao et al., based on ab initio density functional calculations.\textsuperscript{[9y]} By first-principles calculations, Kou et al. also showed that strain and electric field could be used to tune the magnetism in zigzag MoS\textsubscript{2} nanoribbons.\textsuperscript{[9h]} However, in MoS\textsubscript{2} nanosheets, the ferromagnetism induced by vacancy or zigzag edge can be easily removed by local structural rearrangements during annealing or chemical passivation processes.\textsuperscript{[9c,10]} In contrast, doping of transition-metal (TM) elements might provide a way to activate ferromagnetic interactions, if they could substitute for Mo atoms in the MoS\textsubscript{2} nanosheets host.\textsuperscript{[11]} Besides, the TM-doped MoS\textsubscript{2} nanosheets possess tunable magnetic behaviors, due to the engineerable band structures that are partly constituted by 3d electronic states of substitutional TM elements. Although ferromagnetism has been claimed on TM-doped MoS\textsubscript{2} nanosheets using conventional methods,\textsuperscript{[12]} lack of convincing experimental evidence makes it highly suspicious that the ferromagnetism indeed comes from the substitutional TM atoms. The primary reason is that the substitutional TM atoms can be facilely expelled out as metallic clusters by the “self-purification” effect\textsuperscript{[13]} arising from the significantly increased formation energies in the atomically thick nanosheets with strong quantum-confinement. This makes doping TM in nanosheets very challenging, and precipitated metallic clusters may be responsible for the observed ferromagnetism. In addition, weak ferromagnetism could also be activated by the presence of sulfur and/or molybdenum vacancies in MoS\textsubscript{2} nanosheets.\textsuperscript{[14]} Therefore, seeking more efficient routes to prepare TM substitutionally doped MoS\textsubscript{2} nanosheets and confirming the real contributors to the observed magnetic properties are of critical importance in the development of magnetic MoS\textsubscript{2} nanosheets.

In this work, a breakthrough is made by using the supercritical hydrothermal reaction to substitutionally dope Mn ions into MoS\textsubscript{2} nanosheets that show robust ferromagnetic response with a saturation magnetic moment of 0.05 $\mu_B$ Mn\textsuperscript{1/2} at room temperature. This method overcomes the self-purification effect to produce metallic impurities in MoS\textsubscript{2} nanosheets, due to the high supersaturation of the reaction solutions under high reaction temperature (400 °C maximum) and high pressure (22 Mpa) conditions.\textsuperscript{[15]} The substitutional doping is convincingly evidenced by detailed characterizations including high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and X-ray absorption fine spectroscopy (XAFS). In addition, we show that the ferromagnetism of the Mn-doped MoS\textsubscript{2} nanosheets could be tuned by altering the Mn 3d electronic states through intentionally incorporating or removing Li codopants, that is, the saturation magnetic moment increases from 0.05 to 0.11 $\mu_B$ Mn\textsuperscript{1/2} upon Li-incorporation and then reversibly returns to 0.05 $\mu_B$ Mn\textsuperscript{1/2} after Li-removal, confirming the intrinsic nature of the room temperature of the Mn-doped MoS\textsubscript{2} nanosheets and the strong relevance of the magnetic properties with the 3d states of Mn dopants.

The Mn-doped MoS\textsubscript{2} nanosheets were synthesized through a supercritical hydrothermal reaction as schematically shown in Figure 1a, where a maximum reaction temperature of 400 °C and a highest pressure of 22 MPa could be reached. The experimental details are described in the Supporting Information. Under the supercritical hydrothermal reaction condition, the water phase ((NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}·4H\textsubscript{2}O, Mn(CH\textsubscript{3}COO)\textsubscript{2}·4H\textsubscript{2}O), oil phase (CS\textsubscript{2}), and gas phase (Ar) formed a new supercritical phase with a homogeneous S-rich reaction environment. According to the formula $\Delta H = E^i + E_T + (E_{Mo} + \mu_{Mo}) - (E_{Mo} + \mu_{Mo})$, where $E^i$ and $E_T$ are the total energy of the nanosheets with/without the impurity, $E_{Mo}$ and $E_{Mo}$ are the elemental energies of Mo and Mn, respectively, and $\mu$ is related to the range of the chemical potentials in different thermodynamic limits, the formation energy $\Delta H$ of an Mn atom replacing an Mo atom in an MoS\textsubscript{2} nanosheets is significantly reduced in the S-rich reaction environment in which $\mu_{Mo} < 0$.\textsuperscript{[16]} This suggests that the supercritical hydrothermal reaction is energetically favorable for overcoming the self-purification effect and creating substitutional Mn atoms. Under supercritical condition, the reduction of the relative dielectric constant makes the system a high supersaturation to the products to facilitate the simultaneous crystallization and precipitation of S, Mo, and Mn atoms.\textsuperscript{[15b,c,17]}

The morphology and crystal structure of the as-obtained nanosheets can be directly observed by transmission electron microscopy (TEM) images in Figure 1b and Figure S1a in the Supporting Information. Obvious ripples and corrugation can be observed in these images, revealing the ultrathin nature of the nanosheets. Cross-sectional TEM images of curled edges of the nanosheets indicate that the product is four or five atomic-layer thick and the interlayer spacing is 0.63 nm, Figure 1b. The high-resolution TEM (HRTEM) images of the samples (Figure 1c) show distinct lattice fringes of 0.27 nm with 60° angles to the (010) and (100) planes of 2H-MoS\textsubscript{2}, suggesting the primary 2H-MoS\textsubscript{2} phase, in accordance with the X-ray diffraction (Figure S3, Supporting Information) and Fast Fourier Transform (inset of Figure 1c). The energy-dispersive X-ray (EDX) mapping images as shown in Figure 1d–g qualitatively reveal the chemical composition of the nanosheets. Besides the Mo and S elements, the Mn element is obviously detected. Moreover, the inductively-coupled plasma (ICP) analysis yields an Mn/Mo molar ratio of 0.03:0.97, and X-ray photoelectron spectroscopy (XPS) confirms the 2+ valence of Mn (Figure S4, Supporting Information). These results lead us to conclude that Mn\textsubscript{0.03}Mo\textsubscript{0.97}S\textsubscript{2} nanosheets with a 2H-MoS\textsubscript{2} structure were synthesized by the one-step supercritical hydrothermal reaction.

To further identify the location of Mn within the MoS\textsubscript{2} nanosheets, HAADF-STEM and XAFS measurements were performed. In Figure 1h, we can see randomly distributed darker spots in the brighter white (Mo atoms) atomic columns marked by yellow circles. The corresponding cross-sectional intensity of the atom contrast in Figure 1i shows the Mn/Mo intensity ratio of about 1:2, in accordance with the atomic numbers of Mn ($Z = 25$) and Mo ($Z = 42$) elements; the former is expected to have about 50% intensity
of the latter in HAADF.\(^{[18]}\) The atomic-resolution images clearly reveal that the Mn atoms do not form Mn-clusters but are randomly incorporated into the MoS\(_2\) nanosheets by substituting for the Mo sites. Based on the structure model of substitutional Mn in MoS\(_2\) single layer, we simulated the Mo-related HAADF-STEM images and the intensity profiles, which are roughly in agreement with the experimental data (Figure S2, Supporting Information). This is further confirmed by detailed analysis of XAFS spectra. Figure 1j displays the Fourier transformed (FT) curve of the Mn K-edge extended X-ray absorption fine structure (EXAFS) \(k^2\chi(k)\) functions for Mn\(_{0.03}\)Mo\(_{0.97}\)S\(_2\) nanosheets. As references, the Mo and Mn K-edge functions of standard MoS\(_2\) and MnS powders are also plotted. The FT curve of the Mn\(_{0.03}\)Mo\(_{0.97}\)S\(_2\) nanosheets exhibits two prominent coordination peaks at 1.9 and 2.8 Å that are obviously different from the peaks at 2.2 and 3.4 Å for MnS bulk, thus excluding the existence of MnS impurity in the Mn\(_{0.03}\)Mo\(_{0.97}\)S\(_2\) sample. This is also confirmed by the Mn L-edge and S L-edge XANES spectra shown in Figure S5 in the Supporting Information. Moreover, the FT features of Mn\(_{0.03}\)Mo\(_{0.97}\)S\(_2\) are identical to those of the Mn K-edge data of MnS\(_2\), suggesting the substitutional doping of Mn in the 2H-MoS\(_2\) host. It is remarkable that Mn is not merely segregated to domain boundaries compared to the previous works.\(^{[19]}\)

The magnetization (\(M-H\)) curve at 300 K was measured to examine the magnetic characteristics of the as-prepared Mn\(_{0.03}\)Mo\(_{0.97}\)S\(_2\) nanosheets (Figure 2a and Figure S6, Supporting Information). The well-defined hysteresis loop at room temperature demonstrates the room-temperature ferromagnetic behavior of the Mn\(_{0.03}\)Mo\(_{0.97}\)S\(_2\) nanosheets with a coercivity of about 45 Oe and a saturation magnetization of about 0.05 \(\mu_B\) Mn\(^{-1}\) (or 0.05 emu g\(^{-1}\)), significantly higher than \(7\times10^{-4}\) emu g\(^{-1}\) for pure MoS\(_2\) nanosheets (Figure S6, Supporting Information), close to the results reported by Gao et al. and Xia et al. on MoS\(_2\) nanosheets with fluorine adsorption and Cu-doped MoS\(_2\) nanosheets.\(^{[20]}\) From the electron paramagnetic resonance (EPR) spectra (Figure S7, Supporting Information), with the doping of Mn, a typical isotropic hyperfine spectrum with six lines appended to the characteristic peak of sulfur vacancy is clearly observed, which comes from the interaction of Mn\(^{2+}\) electron spin with its nuclear spin of \(I = 5/2\).\(^{[21]}\) This suggests the intimate correlation between the ferromagnetism of Mn-doped MoS\(_2\) nanosheets and the substitutional Mn ions. Considering the low Mn content (\(\approx 3\%\)) in the MoS\(_2\) nanosheets, the room-temperature ferromagnetism Mn\(_{0.03}\)Mo\(_{0.97}\)S\(_2\) nanosheets could hardly be interpreted by the double-exchange mechanism. Alternatively, the bound magnetic polaron model is a promising candidate. According to the concentration (\(\approx 3\%\)) of the Mn dopants in the MoS\(_2\) nanosheets, the mean Mn–Mn interatomic distance is \(\approx 1.4\) nm, smaller than the size of a polaron which is generally <3 nm. Then the spins of the localized defects (S vacancy, see Figure S6, Supporting Information) align those of the nearby Mn ions, producing an effective magnetic field and activating the ferromagnetic interactions.
between Mn ions within the polaron radius (Figure 4a). It is worthy of note that only a small part of the doped Mn ions are located within the overlapped polarons, which explains why the observed saturation magnetic moment \(0.05 \mu_B \text{Mn}^{-1}\) is far below the ideal value (1 \(\mu_B \text{Mn}^{-1}\)) of an \(\text{Mn}^{2+}\) ion.

To further confirm the intrinsic nature of the ferromagnetism in the Mn-doped MoS\(_2\) nanosheets, we examined their magnetic behaviors upon introduction and removal of Li ions. A high-energy ball-milling solid-state reaction was employed to incorporate Li ions into the Mn-doped MoS\(_2\) nanosheets, and Li ions were removed by ultrasonication in HCl solution. As shown in Figure 2a, the ferromagnetic properties of the Mn\(_{0.03}\text{Mo}_{0.97}\text{S}_2\) nanosheets could be reversibly tuned by the strategic incorporation and removal of Li ions. Specifically, incorporating Li ions could significantly increase the saturation magnetic moment from 0.05 \(\mu_B \text{Mn}^{-1}\); after removal of the Li ions, the saturation magnetic moment returns to their original value of 0.05 \(\mu_B \text{Mn}^{-1}\). This reversibility was observed in eight parallel experiments (Figure S8, Supporting Information). Correspondingly, after incorporating Li atoms into the Mn\(_{0.03}\text{Mo}_{0.97}\text{S}_2\) nanosheets, the EPR signal arising from substitutional Mn could track the EPR signal intensity. Although the Li ions incorporation/removal does not change the Mn occupation sites in the Mn\(_{0.03}\text{Mo}_{0.97}\text{S}_2\) nanosheets (Figure 1j), a reversible alteration of the Mn 3d electronic structures could still be observed from the Mn L\(_{2,3}\)-edge X-ray absorption near-edge structure (XANES) spectrum (Figure 3d). After incorporating Li ions, a new peak appears at 639.6 eV in the Mn L\(_{2,3}\)-edge XANES spectrum (Figure 3d), which is restored to the original form after Li ions are removed. Such a change is caused by the charge transfer from alien Li ions to Mn 3d states via the Li\(\equiv\)S bonds, as inferred from the Li 1s XPS (Figure 3a), S 2p XPS (Figure 3b) spectra and the S L\(_{2,3}\)-edge XANES spectrum in Figure 3c and the ultraviolet photoelectron spectroscopy (UPS) results (Figure S9, Supporting Information). The analysis details are given in the Supporting Information. These spectroscopic results then provide further support that the magnetic property of Mn\(_{0.03}\text{Mo}_{0.97}\text{S}_2\) is originated from the substitutional Mn ions, whose 3d electronic states play critical roles in mediating the ferromagnetism of Mn\(_{0.03}\text{Mo}_{0.97}\text{S}_2\) nanosheets.

For an in-depth understanding of the correlation of Mn 3d electronic states with the magnetic behavior of Mn-doped MoS\(_2\) nanosheets, we employed ABINIT software package, which implements density-functional theory using a plane-wave basis set and pseudopotentials, to calculate the electronic structures of both Mn\(_{0.03}\text{Mo}_{0.97}\text{S}_2\) and Li-incorporated Mn\(_{0.03}\text{Mo}_{0.97}\text{S}_2\) nanosheets. The details of the calculations are included in the Supporting Information. The obtained density of states (DOS) are shown in Figure 4b. For the Mn\(_{0.03}\text{Mo}_{0.97}\text{S}_2\) nanosheets, the
The competition between the crystal-field splitting ($\Delta_{\text{cf}}$) and an intratomic (Hund’s) exchange splitting ($\Delta_{\text{ex}}$) makes the Mn 3d orbitals split into a single $a_1$ ($d_{2z^2-r^2}$) antibonding state and two twofold-degenerate $e_1$ ($-d_{xz}$, $-d_{yz}$) and $e_2$ ($d_{xz}$, $d_{yz}$) antibonding states (Figure 4c). Integrating the DOS projected on the substitutional Mn atoms shows that on the average there are a total of 5.18 electrons at the Mn 3d states, where 3.12 and 2.06 electrons occupy the spin-up and spin-down channels, respectively. This suggests that the substitutional Mn in Mn$_{0.03}$Mo$_{0.97}$S$_2$ nanosheets has a $2^{+}$ valence and a magnetic moment of 1.06 $\mu_B$ Mn$^{-1}$ (Figure 4d), in good agreement with the result by Mishra et al.\cite{23} In other words, in Mn-doped MoS$_2$, among the 5 Mn 3d electrons, four electrons occupy the bonding states formed by the hybridization of the Mn 3d orbitals and the neighboring S 3p orbitals, while the last 3d electron occupies the spin-up $a_1$ antibonding state (Figure 4c). With the incorporation of Li ions, the spin-up unoccupied Mn 3d$^{5}$ states are partly occupied (Figure 4c), consistent with the Mn L$_{2,3}$-edge XANES results showing the modified Mn 3d electronic structures (Figure 4b). The Bader charge analysis further shows that on the average about 0.70 e electron is transferred from the Li adatoms to the Mn-doped MoS$_2$ monolayer. At the same time, the partly occupied spin-up $e_1$ states make the magnetic moment in Mn$_{0.03}$Mo$_{0.97}$S$_2$ nanosheets increase to 1.73 $\mu_B$ Mn$^{-1}$ (Figure 4d), and lead to the enhanced saturation magnetic moment in Li-corporated Mn$_{0.03}$Mo$_{0.97}$S$_2$ nanosheets as observed. In contrast, after removing Li ions, the electrons occupying the $e_1$ orbitals are removed, and hence the Mn 3d electronic features are recovered to their original states without Li-incorporation. Hence, our experimental and theoretical results indicate that the reversible procedure of introducing/depleting electrons via Li ions incorporation/removal is the underlying reason for tuning the magnetic behavior of the Mn$_{0.03}$Mo$_{0.97}$S$_2$ nanosheets, which could be used as a drain material in the spin field-effect transistors.

In summary, we have used a supercritical hydrothermal reaction to successfully dope Mn ions into MoS$_2$ nanosheets and obtained robust ferromagnetism at room temperature with a magnetic moment of 0.05 $\mu_B$ Mn$^{-1}$. Detailed study of structural and magnetic properties of the Mn-doped MoS$_2$ nanosheets reveal that Mn ions are substitutionally doped into the MoS$_2$ nanosheets and the magnetic behavior is sensitively reliant on the 3d electronic states of the substitutionally doped Mn. The intrinsically ferromagnetic nature of the Mn-doped MoS$_2$ nanosheets is further supported by the intentionally incorporated or removed Li codopants, which could reversibly tune the ferromagnetism in the as-synthesized nanosheets. Depending on the extent of alien electrons occupying the empty spin-up Mn 3d $e_1$ orbitals, the saturation magnetic moments of the nanosheets exhibit a reversible change, i.e., it increases from 0.05 to 0.11 $\mu_B$ Mn$^{-1}$ and then returns to 0.05 $\mu_B$ Mn$^{-1}$. This work shows that modification of the 3d electronic features of doped ions is an effective pathway for manipulation of the magnetic behavior of 2D magnetic semiconductor materials.
Figure 4. a) Schematic presentation of magnetic polarons. b) Calculated DOS for Mn$_{0.03}$Mo$_{0.97}$S$_2$ nanosheets and Li-incorporated Mn$_{0.03}$Mo$_{0.97}$S$_2$. c) Schematic of the splitting of the Mn 3d orbitals. d) Spin density ($\rho^\uparrow - \rho^\downarrow$) for a single Mn doping atom in a 3 x 3 monolayer MoS$_2$ supercell without (up) and with (down) Li adatom.

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

Acknowledgements
This work was supported by the National Natural Science Foundation of China (Grant Nos. 11435012, U1632263, and 21533007) and the Foundation for Innovative Research Groups of the National Natural Science Foundation of China (11621063). The authors would like to thank Beijing Synchrotron Radiation Facility (BSRF), Shanghai Synchrotron Radiation Facility (SSRF), and National Synchrotron Radiation Laboratory (NSRL) for the synchrotron beamtime.

Conflict of Interest
The authors declare no conflict of interest.


