Nanoscale

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Hydrogen atom induced magnetic behaviors in two-dimensional materials:**Insight on origination in the model of α -MoO₃**

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Abstract: Atomic layered two-dimensional (2D) materials have become fascinating research topics due to their intriguing performances, but the limitation of nonmagnetic properties hinders their further applications. Developing versatile strategies endowing 2D materials with ferromagnetism is one of the main trends in current researches. Herein, a hydrogen plasma strategy is introduced to dope hydrogen (H) atoms into the prototypical layered α -MoO₃ nanosheets, by which the ferromagnetic and exchange bias (EB) effect can be induced by H atom doping into α -MoO₃ to form H_xMoO₃. These effects were interpreted by the density functional theory (DFT) calculations. We find that H atom doping can introduce unoccupied states and induce net magnetic moment localized on the *d* orbital of Mo atom, because of the generated asymmetric distribution of electronic states on Mo atom near the Fermi level. Moreover, the saturation magnetization and the EB field (H_e) of the hydrogenated α -MoO₃ is found to be tunable through the amount of H dopant. This work provides new perspectives for the effective manipulation of ferromagnetism and exchange interaction through H doping. We hope the presented hydrogenation strategy is applicable for other kinds of 2D materials.

Keywords: 2D materials, α -MoO₃ nanosheets, plasma treatment, hydrogenation, ferromagnetism, exchange bias effect.

Introduction

The atomic layered two-dimensional (2D) nanomaterials have been extensively studied for their fascinating electronic properties and potential applications in many fields, *e.g.*, field-effect transistor, integrated circuits and photoelectric devices.¹⁻⁴ However, the non-magnetic properties of most 2D materials may hinder their further applications. For example, α -MoO₃ nanosheets (NSs) can be employed in many smart optoelectronic devices,⁵⁻¹² unfortunately, they cannot be applied to spintronics devices because of the obstruction of nonmagnetic properties. Hence, developing a universal strategy to endow 2D materials with magnetic capabilities is significant for exploring more exciting functionalities and then services for broader applications in diverse spintronic devices.

To date, the traditional magnetic ions doping and vacancies modulation have been used to convert nonmagnetic semiconductors to be ferromagnetic.¹³⁻¹⁵ While for the 2D materials, the strategies, such as phase-incorporation or stress application are being developed for producing desired ferromagnetism.¹⁶⁻²⁰ However, the generated ferromagnetism is unstable and even vanishes easily due to the crystal structure relaxation once the relief of stress.²⁰ Therefore, exploring an advanced approach to activate 2D materials and make them be high-performance magnetic materials become ever more important. Herein, we report the success of transformation of the non-magnetic, layered materials to ferromagnetic by hydrogen plasma treatment, in which the hydrogen (H) atoms can be doped to introduce unpaired electron spins and form a ferromagnetic state. This new hydrogenation strategy is more efficient and

much faster than the Glemser's method in the acidic conditions and thermal treatment by hydrogen gas reported previously.²¹⁻²³

In this study, the layered α -MoO₃ is selected as a prototypical model, in which the H atoms can be successfully doped into the surface/sub-surface layer of α -MoO₃ and form H_xMoO₃ (*e.g.*, hydrogenation process). As a result, the robust ferromagnetism is observed and can be tunable through the amount of H dopant. The generated ferromagnetism is interpreted by the density functional theory (DFT) calculations, and we find that the effect originates from the unpaired electron spin located on the d orbital of Mo atom introduced by the doped H atom. Our findings open a new avenue for tuning the magnetic properties of 2D materials.

Experimental Section

The pristine α -MoO₃ NBs were synthesized by a catalyst-free method using high purity molybdenum wire as precursor.²⁴ In this experiment, a home-made resistive heating setup (ESI Fig. S1) is used, in which the current was applied to the Mo wire through two electrodes at ambient atmosphere for heating and can be controlled by the applied voltage. Then, oxidized Mo nanostructures (α -MoO₃ sheets) would evaporate and deposit on the substrate due to the Joule heat generated by the current.²⁵

The hydrogenation of α -MoO₃ nanosheets was carried out in a home-made plasma enhanced chemical vapor deposition (PECVD) system, in which the flow rate of hydrogen was fixed at 15 sccm. Typically, as-prepared α -MoO₃ nanosheets was placed downstream of the plasma coil inside the tube furnace with the distance of 12.5

cm, where the temperature of the sample was fixed at 180 °C. The hydrogen plasma was activated by 12 MHz radio frequency signal under the pressure of 10 mTorr during the hydrogenation. The hydrogenation time intervals were set at 5 min, 10 min and 20 min, respectively. The pristine and hydrogenated samples were abbreviated as H-0, H-5, H-10 and H-20 according to the hydrogenation time, respectively.

The variation of atomic interactions and crystalline structure of α -MoO₃ before and after H atom doping were analyzed by the Raman spectrum (WITec alpha 300R) and X-ray diffraction patterns (XRD, Philips X'pert Pro MPD). The morphology and chemical composition were characterized by the transmission electron microscopy (TEM, FEI Titan Cs-image, operated at 80 kV) equipped with energy-dispersive X-ray analysis (EDX, Oxford Instrument). The chemical bond information was recorded by the X-ray photoelectron spectroscopy (XPS, VG ESCALAB210), while the variation of magnetic properties of samples was measured by the superconducting quantum interference device (SQUID, Quantum Design MPMS 3-143) magnetometer.

Computational Method

A prototypical model including 4 layers of MoO₃ (128 atoms) was constructed as the framework of this atomic layered structure material (see ESI Fig. S2 for details). The built model can be capable of predicting the difference between the surface and sub-surface hydrogenation as well as the oxygen vacancies originated from the H-plasma treatment. We considered all the possible hydrogenation and oxygen-vacancy positions, and the relative energies regarding different configurations are listed in ESI Table S1 and Table S2. The Brillouin zone of the slabs was described

using $4 \times 4 \times 1$ k -points. All configurations were optimized using the PBE²⁶ level of density functional theory (DFT) calculations using the VASP software.²⁷ The electrons were described using the PAW method²⁸ with a 520 eV energy cutoff. The configurations of valence electrons were considered as $4d^5 5s^1$ for Mo, $2s^2 2p^4$ for O and $1s^1$ for H. The dispersion interactions were described using the Grimme's corrections.²⁹ The optimization criteria were chosen as 10^{-6} eV for energy and 10^{-3} eV/Å for the Heyman-Feynman forces. The spin-polarized calculations were performed to evaluate the magnetization effect of the system.

Results and Discussion

The schematic hydrogenation process is presented in Fig. 1a, where the generated H plasma can be inserted into the crystalline structure of MoO_3 nanosheets (NSs) to form H_xMoO_3 ($x\text{H} + \text{MoO}_3 \rightarrow \text{H}_x\text{MoO}_3$). The success of H atom doping (i.e., hydrogenation) is proved by the Raman spectrum firstly, in which the redshift of the peak of terminal oxygen (Mo=O) stretching mode at 995.1 demonstrates the existence of interactions between M=O bond and H atom (Fig. 1b and ESI Fig. S3).^{6, 30-31} And also, the peak position redshift from 995.1 to 990.6 cm^{-1} as prolonging the hydrogenation time is consistent with the increased amount of H atom. The morphology and structural variations before and after H doping were characterized by the atomic resolution TEM (Fig. 1c-d and ESI Fig. S4). We find that the morphology α - MoO_3 NSs preserves well, and the [101] direction high-resolution TEM image in orthorhombic MoO_3 and H_xMoO_3 also demonstrate the same crystallinity and crystal

structure, as further confirmed by the XRD patterns (Fig. 1g). Both the HRTEM and XRD results indicate the orthorhombic crystalline structure of MoO_3 and H_xMoO_3 ,⁹ which demonstrate that only O-H bonds forms in the H_xMoO_3 after the hydrogen atoms doping while there is no obvious change in crystalline structure. Thus, three salient features we can conclude for the presented hydrogen plasma strategy: i) high efficiency in H atom doping; ii) mild reaction conditions available to maintain the crystalline structure; iii) no impurities formed, which is difficult to be achieved by the well-known Glemser's method.²²

Fig. 1 (a) Schematic of hydrogenation process. The green, red and blue spheres in (a) represent Mo, O and H atoms, respectively; (b) Magnified Raman spectrum of Mo=O bond within $\alpha\text{-MoO}_3$ before and after hydrogenation; TEM and HRTEM images of (c, d) pristine $\alpha\text{-MoO}_3$ and (e, f) hydrogenated $\alpha\text{-MoO}_3$ (H-10); (g) XRD patterns of

α -MoO₃ and those with different hydrogenation time.

The ferromagnetic behavior of H doped α -MoO₃ nanosheets was studied by measuring the magnetization as a function of applied magnetic field (M-H) at room temperature. We find that the hydrogenated α -MoO₃ nanosheets exhibit a robust ferromagnetic, as confirmed by the well-defined hysteresis loops in Fig. 2a. Moreover, the strength of ferromagnetism (saturation magnetization and coercivity) increases with increasing the hydrogenation time. These observations were further supported by the temperature dependent magnetization curves measured with the magnetic field of H=500 Oe (see ESI Fig. S5 for details). This result further supports that the H_xMoO₃ was ferromagnetic although a small paramagnetic contribution from un-coupled spins is observed at low temperatures, while the pristine α -MoO₃ always shows paramagnetic behavior over the whole temperature range with a very weak ferromagnetic signal. The robust ferromagnetism in H_xMoO₃ nanosheets should come from intrinsic properties of the sample, rather than the impurities because there are no magnetic impurities formed in this hydrogenation process, as verified by the identical chemical compositions of the samples in EDX analysis (ESI Fig. S6). Moreover, the ferromagnetism in hydrogenated MoO₃ has good stability due to the thermodynamically stability of H_xMoO₃³²⁻³³. The stability was further proved by the hysteresis loops in the experiment, where there is no obvious difference between fresh H-10 and that after preserved for 30 days (ESI Fig. S7).

To gain an insight into the magnetic properties, we further investigated the field

dependent magnetization at 2 K of zero-field-cooling (ZFC) and field-cooling (FC) under 5000 Oe (Fig. 2b-e). An obvious shift of the center of hysteresis loops was observed towards the negative magnetic field. This phenomenon reveals the existence of the exchange bias (EB) effect at low temperatures, where the exchange bias field (H_e) can be derived from the offset of hysteresis loop along the field. We find that the H_e increases significantly from 4.7 Oe to 127.1 Oe when the hydrogenation time prolongs to 10 min; afterward the H_e decreases if the hydrogenation time was further extended. The variation of saturation magnetization (M_s) and the summarized H_e both demonstrate the tunability of magnetic properties by adjusting the hydrogenation time (Fig. 2f). Meanwhile, the observed EB behavior identifies the coexistence of paramagnetic/ferromagnetic in hydrogenated α -MoO₃, because the exchange anisotropy between different magnetic phases is the necessity for EB effect.

Fig. 2 (a) Hysteresis loops of pristine and hydrogenated α -MoO₃ at room temperature (b-e) $M(H)$ loops of samples at 2 K after zero-field cooling and field cooling (500 Oe) from room temperature. Inset is the magnified curve at the low field, in which the

shift along the field axis shows the EB effect. (f) Variation of derived saturation magnetization and the exchange bias field as the hydrogenation.

The variation of atomic structures in α -MoO₃ and the formation of H_xMoO₃ after the H atom doping were analyzed by the XPS. Without the hydrogenation, 2.4% Mo⁵⁺ exists in the pristine α -MoO₃, as confirmed by the ratio of higher oxidation state (Mo⁶⁺, 3d_{5/2} and 3d_{3/2}) with spin-orbit doublet peaks at the 232.8 eV/236.1 eV and the lower oxidation state (Mo⁵⁺) with doublet peaks at 231.8 eV/234.8 eV in Mo3d core level peaks (Fig. 3a-I). This result demonstrates the sub-stoichiometric characteristic of the pristine α -MoO₃ with low oxygen vacancy concentration, which leads to the observed weak ferromagnetism in Fig. 2a, because the oxygen vacancies can induce the exchange interactions between localized electron spin moments.³⁴ After hydrogenation for 5 min, 6.3% Mo⁵⁺ formed in the α -MoO₃ (Fig. 3a-II), as derived from the broader doublets with a less structured shape (comparing with Fig. 3a-I). With increasing the hydrogenation time to 10 min, the proportion of Mo⁵⁺ increased to 22.2%, and the Mo⁴⁺ in lower oxidation state (with doublet peaks at the 231.5 eV/234.7 eV) appeared, as confirmed by the dominated three spin-orbit doubles in spectra (Fig. 3a-III). Prolonging the hydrogenation time further, the proportion of Mo⁵⁺ and Mo⁴⁺ oxidation state can achieve as high as 21.6% and 21.3%, respectively (Fig. 3a-IV). The increased proportion of Mo⁵⁺ demonstrates the interaction of H with oxygen atom within the MoO₃ to form H_xMoO₃ and then cause a robust ferromagnetism. While the further generated Mo⁴⁺ can give rise to non-magnetic

MoO₂ impurity (Fig. 1h, H-20), and thus the decreased ferromagnetism was observed.

The oxygen state in hydrogenated samples was identified by the *O1s* spectrums. Except for the main peak at 530.8 eV assigned to the typical Mo-O band (Fig. 3b-I), a new peak at 531.6 eV (*i.e.*, Mo-OH) appeared and became stronger as increasing the hydrogenation time (Fig. 3b, I-IV). It fully confirms the generation and increment of the hydroxyl group. The varied oxidation states of Mo and the proportion of Mo-O/Mo-OH further reveal that the oxidation state of Mo was changed as H atom doping and then the Mo-OH can be generated (Fig. 3c-d). Thus, the formation of H_xMoO₃ on MoO₃ and the exchange interaction between MoO₃ and H_xMoO₃ should be the origination of the ferromagnetism and EB effect in hydrogenated MoO₃, respectively. Comparing the proportion of Mo⁵⁺ and -OH group in the samples, it can be found that the concentration of Mo⁵⁺ is slightly higher than -OH group. For example, the proportion of Mo⁵⁺ is about 22.2 % in H-10 sample while the proportion of -OH group is 17.7 %. In principle, 17.7 % H-atom dopant can generate 17.7 % Mo⁵⁺ due to the valence conservation. Herein, the proportion of Mo⁵⁺ is 4.5% higher than that of OH group, and this is because of the oxygen vacancies in the sample. Hence, we can calculate that the oxygen vacancy induced by the H plasma treatment is only 2.1% after the reduction of 2.4% Mo⁵⁺ in the pristine MoO₃. These data demonstrate the efficiency of hydrogen plasma strategy to dope H atom in α -MoO₃. Moreover, the variation of magnetic behaviors in Fig. 2f, the concentration of Mo⁵⁺(Fig. 3d) and hydroxyl group (Fig. 3d) display the same trend as the hydrogenation time, and this result confirms that the magnetic properties of α -MoO₃

strongly depend on the amount of H dopant.

Fig. 3 X-ray photoelectron spectroscopy of (a) Mo 3d core level spectra and (b) O 1s of α -MoO₃, H-5, H-10 and H-20. The varied oxidation state of (c) Mo and (d) the proportion of Mo-O/Mo-OH in the samples as the hydrogenation time.

The origination of magnetic behaviors of MoO₃ and H_xMoO₃ were further interpreted by the density functional theory (DFT) computations³⁵. As demonstrated in the experiment, doping of hydrogen atoms into the layered α -MoO₃ may lead to two kinds of structures: 1) forming O-H bonds and leading to H_xMoO₃; 2) forming H₂O molecules and leading to oxygen vacancies but with a tiny amount (~2%). Hence, we built prototypical models (ESI Fig. S2) considering all possible doping positions within surface/sub-surface, and then studied the correlations between hydrogen dopant and magnetic properties of the hydrogenated α -MoO₃. The relative energies regarding all the configurations are listed in ESI Table S1 and Table S2. Since the terminal oxygen (O_t) is not fully saturated, doping of hydrogen at the

surface/sub-surface O_t can obtain more stable structures. The latter one may form an additional hydrogen bond with the oxygen in the intermediate layer, leading to an even more stable structure. On the other hand, generating oxygen vacancies at the bridging positions (O_a or O_b , ESI Fig. S8 and Fig. S9) may break several Mo-O bonds, and therefore, are energetically less stable compared with other possible vacancy positions.

Fig. 4 (a) Calculated density of state (DOS) structure for $\alpha\text{-MoO}_3$ model with (I) perfect structure, (II) one oxygen vacancy (surface O_t site) and (III) one hydrogen dopant (sub-surface O_t site). All models are the configurations with the lowest energy. The lateral view of $\alpha\text{-MoO}_3$ model with (b) one oxygen vacancy and (c) one hydrogen dopant. The yellow shells in (b) and (c) represent the localized unpaired electrons. (d) Schematic ferromagnetic formation mechanism in hydrogenated

α -MoO₃.

Thereafter, the electronic properties of defective pristine α -MoO₃ and H_xMoO₃ were explored using the DFT calculations. In general, the perfect MoO₃ does not have net magnetizations (Fig. 4a-I), while the oxygen vacancies can introduce unoccupied states and induce net magnetic moment localized on the *d* orbital of Mo atom (Fig. 4a-II and b), because of the generated asymmetric distribution of states on Mo atom below the Fermi level. Also, the doping of hydrogen atoms at different levels to form H_xMoO₃ can introduce asymmetric properties of electronic densities, leading to a certain magnetic effect on the MoO₃, as demonstrated by Fig. 4a-III. Due to the inherent properties of layered MoO₃, the unpaired electrons can be highly localized around Mo atoms, where the *d*-orbitals of the Mo atoms can hold most of the net magnetizations without interrupting other atoms. Hence, accumulation of more hydrogen dopants into the system may gradually increase the magnetic properties of this material, which is consistent with our experimental results. The ferromagnetic formation mechanism was illustrated in Fig. 4d, where the polarized spins were induced by the intercalated H or oxygen vacancy localized around the Mo atom. The exchange interaction between the neighboring spins makes them align along a direction and then give rise to ferromagnetism. Thus, the DFT simulations and experimental results both confirm that the reason of the enhanced ferromagnetism in H_xMoO₃ mainly comes from the introduced H atoms, while the contribution of oxygen vacancies is limited due to the low concentration.

Conclusion

In summary, we present a new hydrogen plasma strategy to endow the nonmagnetic 2D materials with magnetic properties. The typical layered α -MoO₃ nanosheets is selected as a model, in which the unpaired electron spin was introduced by the H atom doping and then give rise to the robust ferromagnetism and EB effect. The studies of the structural variation and magnetic properties of the hydrogenated α -MoO₃ reveal that the formed H_xMoO₃ is the cause of the ferromagnetism. While the H atom induced asymmetric properties of electronic densities and the spin polarization localized at the *d* orbit of the Mo atom was further confirmed to be the magnetic origination by the DFT calculations. We hope that the introduced hydrogenation strategy with H atom doping is feasible to manipulate other kinds of 2D materials for more capabilities and higher performances.

Acknowledgments

This work was supported by National Natural Science Foundation of China (11604130, 51601082, 51771085), the Fundamental Research Funds for the Central Universities (lzujbky-2015-304 and lzujbky-2015-305) and Open Project of Key Laboratory of Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University (LZUMMM2018013).

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The magnetic behaviors are successfully modulated in a prototypical layered $\alpha\text{-MoO}_3$ nanostructures by doping H atom and forming H_xMoO_3 .