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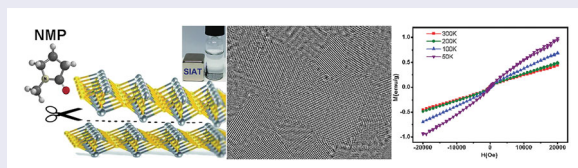
Toward edges-rich MoS₂ layers via chemical liquid exfoliation triggering distinctive magnetism

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ABSTRACT

The magnetic function of layered molybdenum disulfide (MoS₂) has been investigated via simulation, but few reliable experimental results have been explored. Herein, we developed edges-rich structural MoS₂ nanosheets via liquid phase exfoliation approach, triggering exceptional ferromagnetism. The magnetic measurements revealed the clear ferromagnetic property of layered MoS₂, compared to the pristine MoS₂ in bulk exhibiting diamagnetism. The existence of ferromagnetism mostly was attributed to the presence of grain boundaries with abundant irregular edges confirmed by the transmission electron microscopy, magnetic force microscopy and X-ray photoelectron spectroscopy, which experimentally provided reliable evidences on irregular edges-rich states engineering ferromagnetism to clarify theoretical calculation.



IMPACT STATEMENT

- Edges-rich MoS₂ layers are achieved via chemical liquid approach.
- The abundant edges MoS₂ nanosheets demonstrate highly superior magnetic property, which provides reliable evidences to identify irregular edge states engineering ferromagnetism experimentally.

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KEYWORDS

Edges-rich MoS₂; exfoliation; magnetic property; grain boundaries

Introduction

Intense interest has been paid on the atomically thin two-dimensional transition metal dichalcogenides (TMDs), triggering distinctive properties (electronics, optoelectronics, and magnetism), which can dramatically differ from those of the corresponding bulk crystals [1–8]. Representatively, the advances on the edge-dependent of molybdenum disulfide (MoS₂) have rendered in applications of electric devices, photovoltaic cell, photo-catalyst and semiconductors [9–19]. Very recently, the strain effects of low-dimensional materials were carried out

dramatically to understand their electric/magnetic properties [20,21]. Particularly, the magnetic function of MoS₂ nanosheets was evaluated and tuned and by applying the strain effects via the first-principle simulations [22,23].

According to the directions of termination, there existed two kinds of edges: armchair and zigzag states. Pan H. et al. proposed the essence of the ferromagnetism in MoS₂ with zigzag edges. It reported that the magnetic properties of MoS₂ nanosheets can be evaluated by simulating the energy difference between the nonmagnetic

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and magnetic states [24,25]. The energies of nonmagnetic states in armchair edges were equal to those of magnetic states, exhibiting nonmagnetic activity. Comparably, the energies of nonmagnetic states in zigzag edge structures were higher than those of magnetic states, demonstrating the typical magnetic property [26–29]. The calculations illustrated that the MoS₂ nanosheets with armchair edges were nonmagnetic while these of zigzag edges were magnetic.

Theoretically, it has been reported that zigzag-edged graphene nanosheets have localized electrons at edge carbon atoms [30–34]. And there was ongoing work by Chen et al. presenting the distinctive magnetism of graphene with irregular zigzag edges experimentally [35]. Comparably, Magnetic MoS₂ layers should be more suitable for spintronic potentials than graphene because ferromagnetic graphene can only be achieved by applying external electrical/magnetic field, thus the magnetic moments/states of zigzag MoS₂ would be higher/stronger than those of graphene nanosheets. Terrones calculated that the zigzag MoS₂ nano-ribbons exhibited extraordinary magnetic properties even if the ribbons were passivated with hydrogen atoms [25]. However, there have not been a few works that supported experimentally, but only Gao et al. mentioned the intrinsic ferromagnetism of MoS₂ nanosheets was related to the presence of edge spins [36]. Han et al. employed proton irradiation or annealing in the hydrogen condition to induce the ferromagnetic order from diamagnetic MoS₂ crystals, resulting in an promoted transport property [37].

Here, we explored single, double and multi-layered MoS₂ via chemical liquid approach by means of intensive sonication, harnessing to exfoliate or delaminate atomic nanosheets (Figure 1 and experimental section in details). Previously, we have demonstrated this approach to exfoliate hexagonal boron nitride (h-BN) and layered graphene (G), creating artificially building blocks as stacked h-BN/G hybrids [38]. It allowed the confinement of electrons upon exfoliation leading to unprecedented magnetic and electrical properties. Particularly, the edge-dependent magnetism was superior to exhibit with the advances on the abundant edges MoS₂ nanosheets. Additionally, it can be scaled up the exfoliation process with high yield, expecting to explore more potential applications in electromagnetism devices, and pave the way for magnetic development of 2D MoS₂.

Experimental

Preparation of single-, double- and multi-layered MoS₂. MoS₂ powders were purchased from Sigma Aldrich; N-methyl-pyrrolidone (NMP) and isopropanol (IPA) solvents were purchased from Aldrich and used as supplied.

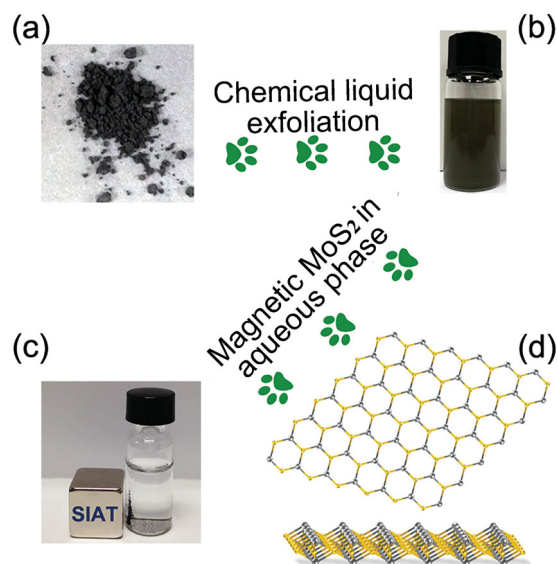


Figure 1. Schematic depiction of the exfoliated MoS₂ with magnetism via chemical liquid strategy. (a) Bulk MoS₂ powder with size around 1.0 μm. (b) A dispersion of exfoliated MoS₂ in IPA solution. (c) Layered MoS₂ nanosheets dispersed in water, demonstrating the ferromagnetism clearly. (d) Atomic layer MoS₂ arrangement of S and Mo atoms model.

All other reagents and solvents were of analytical grade. Pristine MoS₂ powder dissolved in NMP solvent (initial concentration of 0.5 mg/ml) sonicating in a low power sonic bath (Fisherbrand FB15061, 750 W) for 4 h. Then the above mixture was transferred to a higher power sonicator (Coleparmer 1200 W) and continually to be sonicated for 6 h. Finally, the mixture was centrifuged at 3000 rpm for 40 min, the supernatant was collected by pipette and filtered with filtration system. The above-filtered flakes of MoS₂ nanosheets were then dispersed into IPA uniformly, then dried at 60°C, finally, the exfoliated MoS₂ nano-layers containing single, double and multi-layered (less than 10 layers) were stored in vacuum to be investigated further characteristics. The obtained MoS₂ layers were dissolve into aqueous solution to evaluate their dispersity and magnetic separation by placing a magnet aside (Figure 1(c)).

Instrumentation

Transmission electron microscopy (TEM), high-resolution bright-field (HRTEM), high angle annular dark-field (HAADF) images and energy-dispersive X-ray spectroscopy (EDS) measurements were carried out with the field emission FEI-F30, operated at 200 kV. X-ray photoelectron spectroscopy spectra (XPS) data were taken by Thermo ESCALAB 250XI Multifunctional imaging electron spectrometer, which was equipped with

a Al K α source. XPS data was analyzed with the MultiPak software. Raman spectroscopy was used to characterize the structure of the film at 514 nm laser excitation. Optical absorbance measurements (Shimadzu ultraviolet-3600) were performed using 1 cm quartz. X-ray diffraction (XRD) with Rigaku D/Max Ultima II Powder XRD configured with a vertical theta/theta goniometer, Cu K α radiation, graphite monochromator, and scintillation counter. The hysteresis loop character was measured using the DH4516N Dynamic hysteresis and analyzed with Magnetic Data Analysis Solution (MDAS). The physical property measurement system (PPMS) was carried with the model P525 vibrating sample magnetometer (VSM). All samples were loaded into the typical nonmagnetic capsule supported by Quantum Design Company to investigate the VSM (please see the

supporting information S1 for more detailed measurement). Magnetic force microscope (MFM) and atomic force microscope (AFM) measurements were conducted by the Dimension 3100, Veeco. The UV-vis absorbance spectrum was conducted with the PerkinElmer Lambda 750 absorption spectrophotometer. All above data was plotted and analyzed by using Origin-Pro 8 software.

Results and discussion

Individual and multi-layered MoS₂ nanosheets were observed via TEM and HRTEM as shown in Figure 2(a) and (b). The insight of edges-rich structural MoS₂ layers was obtained with scanning transmission electron microscopy (STEM) image (Figure 2(c)), indicating the hexagonal atomic arrangement, the insert in Figure

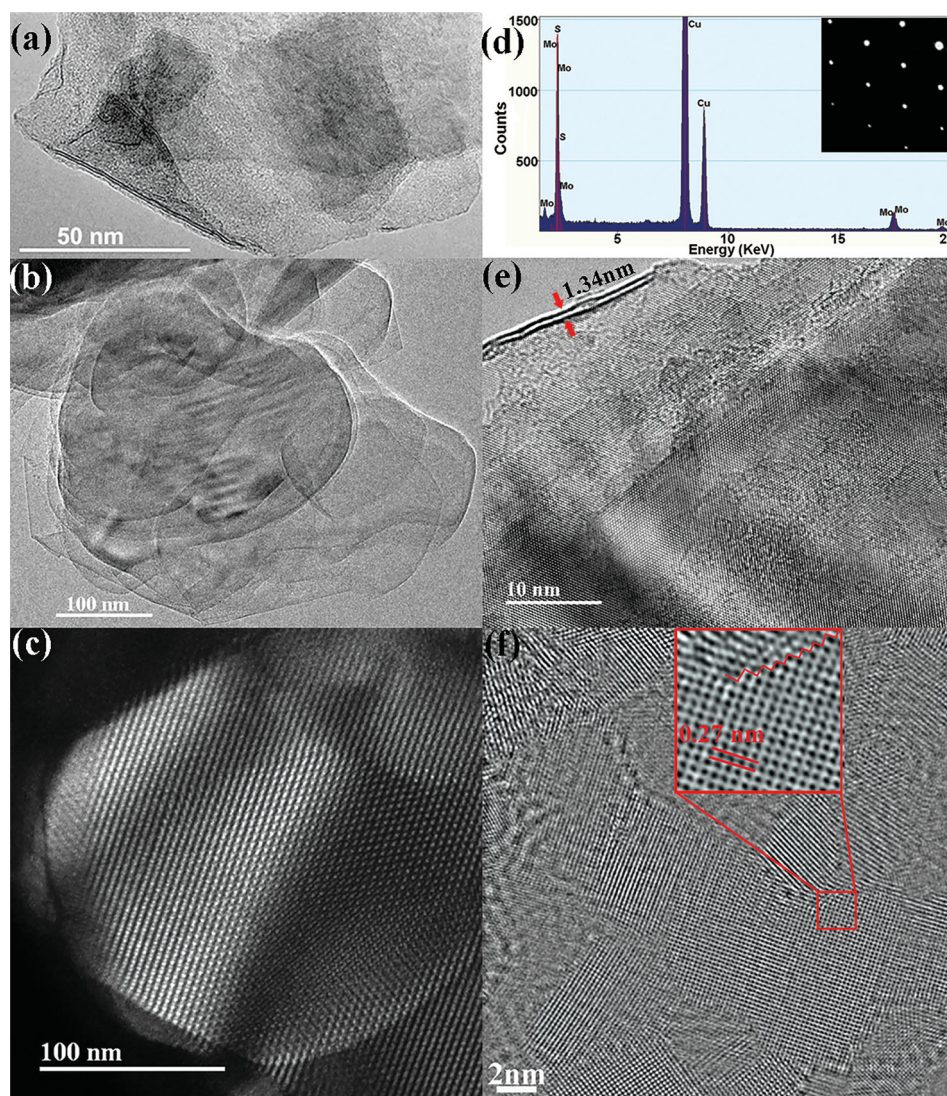


Figure 2. Morphology and lattice structure of edges-rich MoS₂ layers. (a) and (b) TEM images of the exfoliated MoS₂ layers. (c) HAADF image of single layer MoS₂ nanosheet. (d) EDS image of exfoliated MoS₂ layers, and insert was the SAED pattern. (e) and (f) High-resolution bright-field TEM images of single and double layers MoS₂. The region indicated by square was enlarged to show the edges and basal plane hexagonal structures.

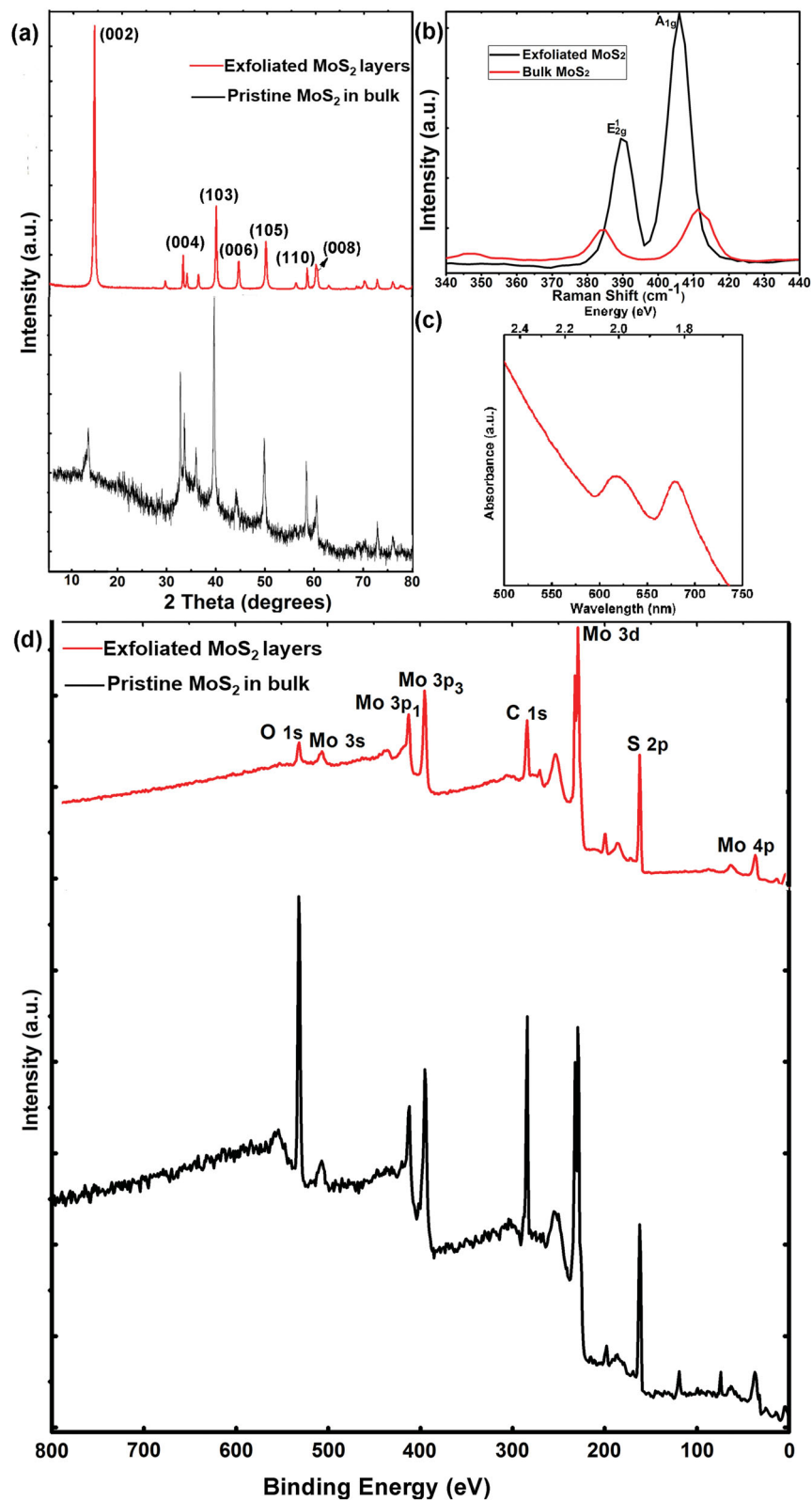


Figure 3. Evidence for exfoliated edges-rich MoS₂ structure. (a) XRD pattern taken on the exfoliated MoS₂ nanosheets and bulk MoS₂. (b) Raman spectra captured on the exfoliated MoS₂ and pristine MoS₂ in bulk. (c) UV-vis absorption spectrum of exfoliated MoS₂. (d) XPS spectrum of the exfoliated MoS₂ nanosheets and bulk MoS₂ for full scanning.

2(d) was selected area electron diffraction (SAED) pattern corresponding with the STEM measurement. It was essential to point out that there were single, double and multi-layered (less than 10 layers) existed in this typical exfoliation system via chemical liquid approach. The EDS provided more evidence on elements analysis of atomic MoS₂.

The number of MoS₂ layers can be identified from the edge state as shown in Figure 2(e), there were two layers of exfoliated MoS₂ with the thickness of 1.34 nm. The interplanar spacing of 0.27 nm can be directly measured from the high-resolution TEM image (Figure 2(f)), which was consistent with *d* spacing of hexagonal MoS₂ (100) planes. Moreover, the grain boundaries appeared obviously on the basal surface of exfoliated MoS₂, enlarged by square in red line. It was fundamental to achieve the understanding of edges-dependent magnetic property; there were more high-resolution TEM images of layered MoS₂ in the supporting information S2, expecting to provide a feedback on the morphology of exfoliated MoS₂ layers for the correlated activity.

XRD was carried out as shown in Figure 3(a); the strong diffraction peak (002) revealed the higher crystallinity of exfoliated MoS₂ compared to that of the

pristine MoS₂ in bulk. Other minor diffractions, such as (004), (103), (006), (105), (110) and (008) existed obviously, implying the nanoscaled crystallites in different orientations. Furthermore, the full width at half maximum (FWHM) value of the (002) diffraction peak was calculated by using the *Scherrer Equation*, and we estimated the thickness of MoS₂ planes along the *c* axis around 2.1 nm, which was approximately equal to three layers according to the interlayer spacing of 0.63 nm, corresponding to the result of HRTEM measurement.

Further structural characterizations were obtained by Raman spectroscopy with a 532 nm laser excitation. Figure 3(b) demonstrated Raman spectra of exfoliated MoS₂ nanosheets (blank line), the peaks located at 389.4 and 405.9 cm⁻¹ were identified as *E*_{2g}¹ and *A*_{1g} modes, which were associated with vibrations of Mo and S atoms in the basal plane and out-of-plane respectively. The frequency of the *E*_{2g}¹ vibration exhibited red shift, while *A*_{1g} mode appeared blue shift compared to these of MoS₂ in bulks (*E*_{2g}¹ at 385.1 eV and *A*_{1g} at 411.3 eV in red line). It indicated that the rate of frequencies for both two modes demonstrated a slight variation with the thickness decreasing of exfoliated MoS₂. For films of more than five layers, the frequencies of both modes converged

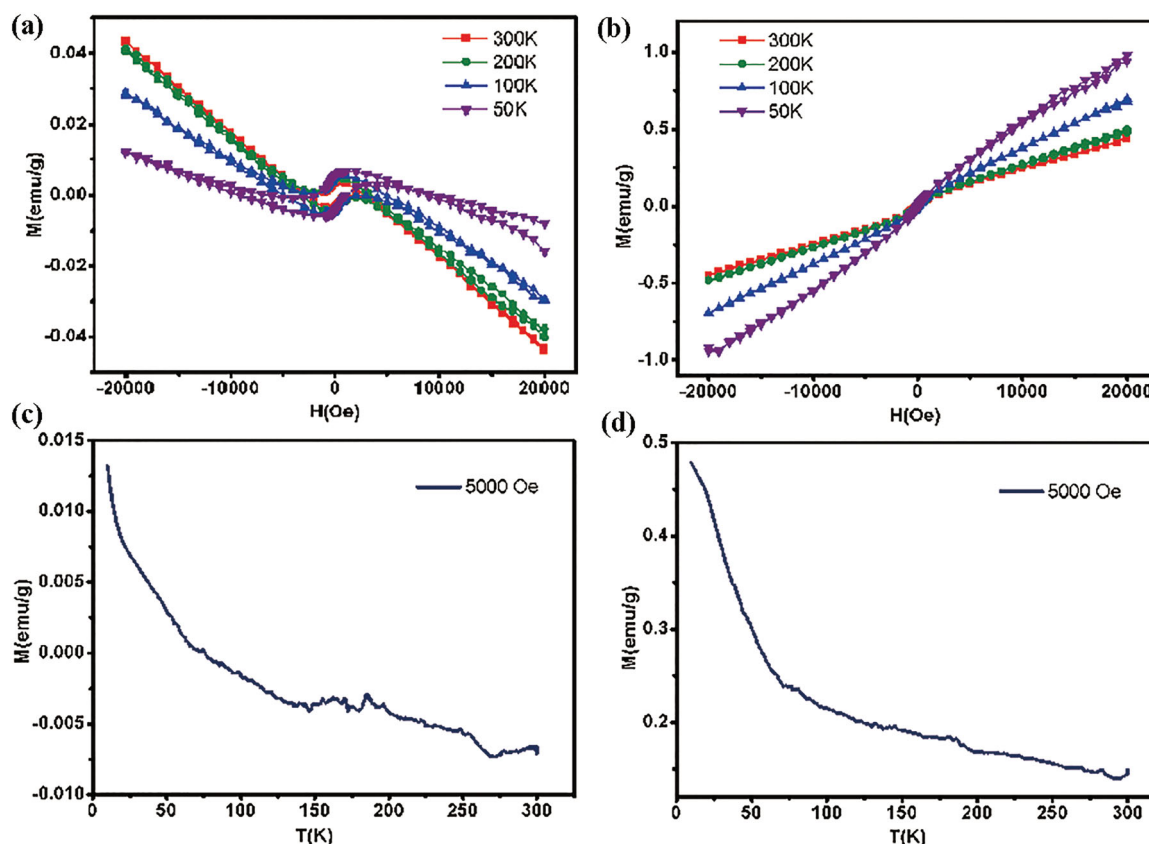


Figure 4. Magnetic evidence for pristine bulk MoS₂ and exfoliated edges-rich structural MoS₂. Magnetization (*M*) vs. applied field (*H*) data taken at different temperatures with field parallel for (a) pure bulk MoS₂ and (b) layered MoS₂ basal planes. (c) Magnetic susceptibility of pristine MoS₂. (d) Magnetic susceptibility of exfoliated MoS₂ nanosheets.

to the bulk values. We evaluated that the numbers of layered MoS₂ were less than three layers according to previous report [39]. In addition, the absorption spectrum of monolayer MoS₂ was plotted to investigate the optical property compared to the pristine bulk MoS₂ without UV-vis absorption. The two principal absorption features at 615 and 678 nm were associated with the A and B excitations of MoS₂ (Figure 3(c)). XPS illustrated characteristic Mo and S peaks respectively, revealing the high purity of ultrathin MoS₂ without any other magnetic impurity as shown in Figure 3(d). In comparison, there was not obvious difference from XPS survey between the exfoliated MoS₂ and bulk MoS₂ except for rather stronger peaks of O and C in pristine MoS₂, which indicated some interaction with air and carbon contamination on the surface of measured sample.

The magnetization (M) vs. temperature (T) measurements were conducted to prove the magnetism of obtained MoS₂ layers in detail. There was an obvious diamagnetic signal shown in Figure 4(a), indicating that the diamagnetism was dominated in bulk MoS₂. However, the clear ferromagnetic parts in exfoliated MoS₂ nanosheets were observed in Figure 4(b), which

demonstrated the ferromagnetic function in edges-rich structural MoS₂ nanosheets even though the diamagnetic and paramagnetic background superimposing in some extent. The magnetic susceptibility of pristine MoS₂ and exfoliated MoS₂ nanosheets was plotted respectively as shown in Figure 4(c) and (d). The susceptibilities were determined from the slope of $M(H)$ curves taken at the particular temperatures. There was no long-range magnetic ordering existed in the bulk sample, which illustrated the diamagnetic property. However, the magnetic susceptibility of layered MoS₂ demonstrated typical long-range magnetism, and obviously the magnetization of exfoliated MoS₂ nanosheets was over 10–40 times superior to the bulk MoS₂ comparing with the value of curves.

$M(H)$ curves were magnified magnetization at low field to observe the coercivity dependency in temperature at 10, 100 and 300 K shown in the Figure 5(a)–(c). And it exhibited that the coercive fields were clearly observed in different temperatures, up to 261, 85, 68 Oe respectively, and the coercive field was in decline trend with the temperature increasing, which supplied a strong evidence for the ferromagnetic signal existed in the layered MoS₂. In addition, the zero field cooling (ZFC)/field cooling (FC)

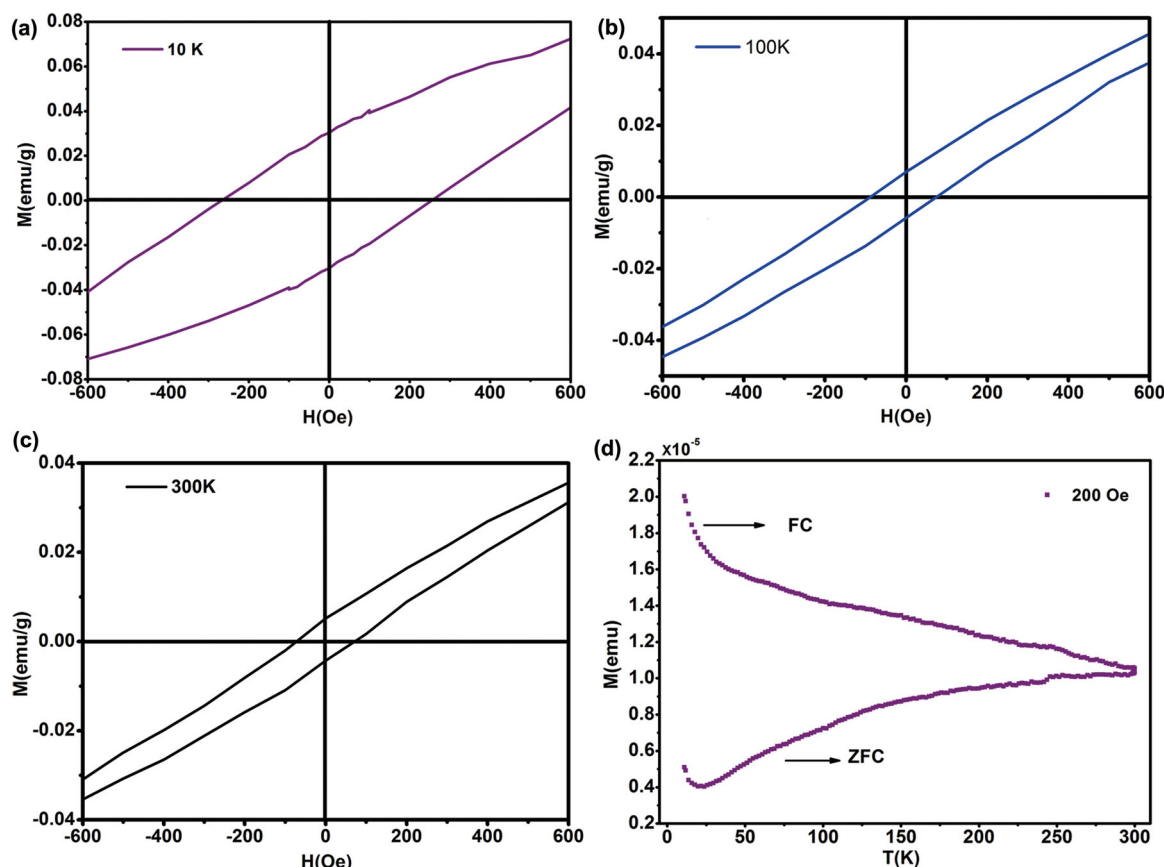


Figure 5. Magnetic evidence for exfoliated edges-rich structural MoS₂. Curves are magnified magnetization at low field to observe the coercivity dependency in temperature at 10, 100 and 300 K of exfoliated MoS₂ nanosheets (a)–(c). (d) The ZFC/FC curves of the layered MoS₂ measured at 5000 Oe.

curves of the layered MoS_2 were measured at 5000 Oe as shown in Figure 5(d). The bifurcation phenomenon between ZFC and FC curves was quite obvious, illustrating the ferromagnetism of layered MoS_2 nanosheets. This particular magnetism phenomenon was possibly triggered due to the exfoliation of MoS_2 with edges structure via chemical liquid. Mostly, this ferromagnetic property was controlled by their inter-atomic distances, and edges structure, furthermore considerable zigzag edge structures located in the grain boundary [35], where the magnetic property was induced. Particularly, the creation of MoS_2 triple vacancy resulted in a significantly magnetic moment in this system [18]. This clearly indicated edge structures or basal plane dislocation during exfoliation using chemical liquid, exhibiting ferromagnetic property in the exfoliated MoS_2 nanosheets, which was consistent with the TEM measurements.

Magnetic force microscopy (MFM) was a typical mode of the noncontact scanning force microscopy, which was an important analytical technique for the near-surface stray-field variation of magnetic materials. It was recognized that the detection of magnetostatic interactions at a local scale was possible by equipping the force microscope with a ferromagnetic probe [40,41]. Firstly,

we captured the surface morphology of layered MoS_2 by atomic microscopy force (AMF) as shown in Figure 6(a), the thickness of exfoliated MoS_2 was estimated to about 2.1 nm averagely, three layers of MoS_2 nanosheets approximately (Figure 6(b)). Then MFM image showed that the exfoliated MoS_2 demonstrated a strong magnetic activity (Figure 6(c)).

The absorption force as well as repulsive force appeared during the interaction coupling of the ferromagnetic probe and the stray-field produced by exfoliated MoS_2 . As the magnetization directions of probe and sample domain structure were opposite, then the interaction force exhibited attractable which was an absorption force presenting dark contrast in MFM image. On the contrary, Figure 6(c) demonstrated bright contrast, which illustrated the repulsive interaction between the probe and exfoliated MoS_2 sample domain structure. Figure 6(d) showed three-dimensional image of magnetic layered MoS_2 ; the bright contrast can be observed clearly. However, the magnetic domain structure (especially the edges) could not be captured obviously in the MFM image; it might be caused by factors such as the magneto-crystalline anisotropy and magnetostriction energies. Additionally, lattice defects, stresses and

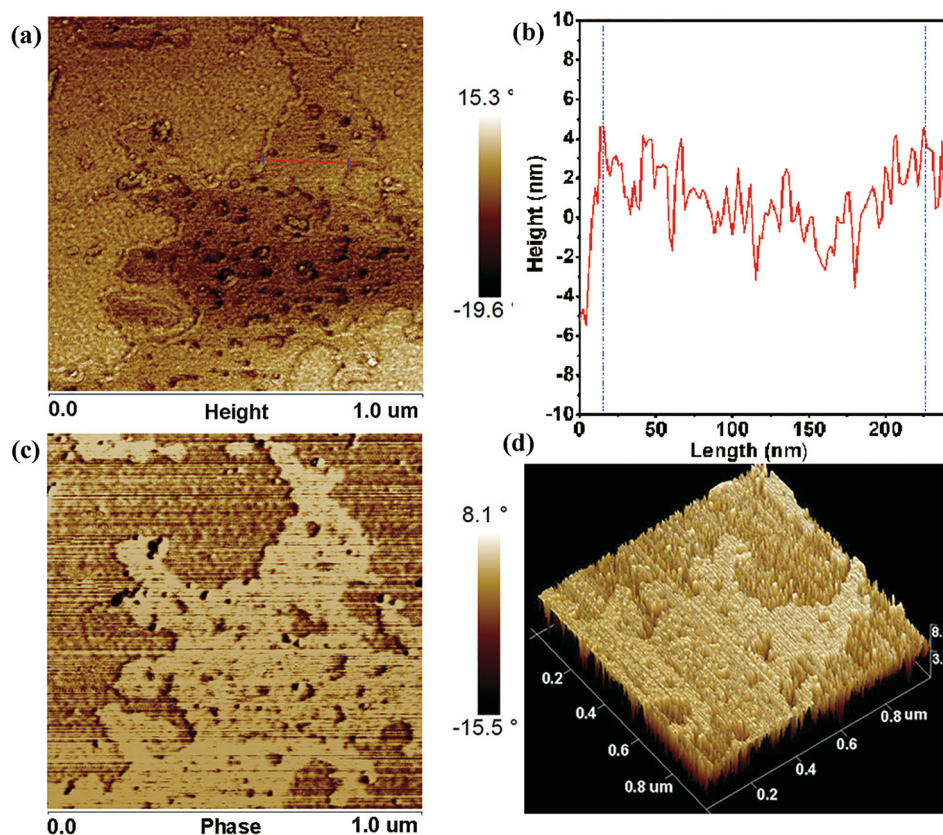


Figure 6. (a) AFM image taken on layered MoS_2 nanosheets tracks of 1.0 μm periodicity. (b) Thickness of the layered MoS_2 nanosheets with red line in image (a). (c) MFM image taken on layered MoS_2 nanosheets tracks of 1.0 μm periodicity, with the lifting the cantilever probe up to 30 nm from the sample surface to measure a long-range interaction. (d) The 3D image of (b).

the surface topology exhibited an additional influence on the domain structure. It was necessary to explore magnetic domain structure in exfoliated MoS₂ nanosheets. Interestingly, there were vacancies exposed crossing the full-scale film in MFM images, the possible reason was that we captured several layered MoS₂ nanosheets in a large scale parallel length of 1 μ m, so that the presence of defects including atomic vacancies, displacement can be demonstrated in the MFM condition due to the color variation with the depth of tested film.

Herein, we found that the ferromagnetic performance of exfoliated MoS₂ nanosheets was dependent on the amount of edge sites and size, which played a significant role on triggering typical magnetism. There were plenty of edge sites observed which could provide more localized defects or vacancies prompt. Then the spins of the localized defects aligned these of the nearby electron carriers, which produced an effective magnetic field and activated the ferromagnetic performance. Therefore, we addressed the chemical liquid assisted with robust sonication to endow more edge sites or smaller size of exfoliated MoS₂ nanosheets, expecting to be generalized to tune the magnetic properties of other two-dimensional nanosheets.

Conclusion

In summary, a comprehensive analysis focused on the exfoliated edges-rich MoS₂ layers via chemical liquid strategy revealed their intrinsic ferromagnetism. The magnetic measurements illustrated the clear ferromagnetic property of exfoliated MoS₂, in contrast to the pristine MoS₂ in bulks showing diamagnetism. This was attributed to the presence of edges-rich structure on grain boundaries, which was confirmed by the TEM, XPS and MFM investigations. However, the results of MFM images could not capture a strong direct proof on the edges state magnetism due to the resolution of MFM facility; we expected to explore further analysis and to provide reliable evidences which would identify the irregular edge states engineering ferromagnetism. Additionally, the coupling of spin and dislocations might exist during exfoliation with intense sonication, triggering the magnetic property, and it was essential to explore further simulation for ferromagnetic mechanism of exfoliated MoS₂ with zigzag edges structure theoretically.

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