Room-temperature ferromagnetism of single-crystalline MoS_2 nanowires

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Single-crystalline molybdenum disulphide (MoS_2) nanowires are prepared by a hydrothermal method. The single-crystalline MoS_2 nanowires display substantial ferromagnetism at room temperature. The S vacancies and Mo-edges are possible mechanisms responsible for the observed ferromagnetism at room temperature.

1. Introduction: Solid molybdenum disulphide (MoS_2) has a distinct layered structure, in which each Mo layer is sandwiched between two sulphur layers [1–5]. Bulk MoS_2 has wide applications in the fields of solid lubricants [6–8], catalyst [9, 10] and energy storage [11]. Since the hexagonal layered structure of MoS_2 is similar to that of graphite [1], mechanical exfoliation has been successfully applied to isolate the monolayer MoS_2 [12–14]. The monolayer MoS_2 has also been grown on a Cu substrate [15]. The success in isolating the monolayer MoS_2 renders the fabrication of one-dimensional MoS_2 nanostructures such as MoS_2 nanoribbons and single-walled MoS_2 possible [14, 16–20]. Unlike graphene, which is a zero-gap semi-metal or bulk MoS_2 which is a semiconductor with an indirect gap, the monolayer MoS_2 has been shown by both experiments and first-principles calculations to be a semiconductor with a direct bandgap [12, 21–23]. The direct bandgap character opens the possibility for the application of the monolayer MoS_2 as transistors [14, 16, 17, 21, 24], light-emitting diodes and solar cells.

Bulk MoS_2 is known to be a non-magnetic material. Compared with bulk materials, low-dimensional nanostructured materials have special physical properties, which is because of their anisotropic property and a unique size effect. Recent studies on the magnetic response of MoS_2 are limited to theoretical calculations [25–28]. These calculations predicted ferromagnetism in MoS_2 in the presence of zigzag Mo-edges [25–27] and sulphur vacancies [28]. From this point of view, in the presence of zigzag edges, magnetism should be observed in MoS_2 nanoribbons, nanocrystalline thin films and even in bulk limit provided that the average grain size is small enough. Ferromagnetism was observed in MoS_2 thin film [29] and MoS_2 bulk [30] with small grain size at room temperature, which was attributed to the existence of the zigzag edges in the ferromagnetic ground state.

To the best of our knowledge, the magnetic properties of single-crystalline MoS_2 nanowires have not yet been reported. In this Letter, we report ferromagnetism of single-crystalline MoS_2 nanowires at room temperature.

2. Experimental

2.1. Synthesis of MoS_2 nanowires: MoS_2 nanowires were prepared by a hydrothermal process. All chemicals used in this work were of analytic purity. In a typical procedure, 2.5 mmol of $Na_2MoO_4{\cdot}2H_2O$ and 5 mmol of CH_4N_2S were dissolved in 35 ml of distilled water, and then 3.5 ml concentrated hydrochloric acid was added into the reaction solution under violent stirring. The resulting solution was transferred into a 50 ml Teflon-lined stainless autoclave and tightly sealed, which was kept at 220°C for 36 h. Then the autoclave was allowed to cool to room temperature naturally. The resulting products were filtered off, washed with distilled water and absolute ethanol several times and dried in vacuum at 60°C for 12 h for characterisation.

2.2. Characterisation: The microstructure of MoS_2 nanowires was characterised at room temperature by X-ray diffraction (XRD, Shimadzu XRD-7000 X-ray diffractometer) with Cu Kα radiation. The surface morphology of the MoS_2 nanowires was characterised using a scanning electron microscope (SEM, JSM-6510). The size and crystal structure of the MoS_2 nanowires were observed by transmission electron microscopy (JEM-2100). The magnetic properties were characterised by a vibrating sample magnetometer from the Microsense Corporation, USA.

3. Results and discussion: The powder XRD pattern of the samples is shown in Fig. 1*a*. It can be seen that the diffraction peaks are indexed as MoS_2. The peaks with *d* spacing of 6.4, 2.7, 1.6 and 1.2 Å correspond to the (002), (100), (103) and (110) reflections, respectively, of nanostructured 2H-MoS_2 (JCPDS 37–1492). Meanwhile, the peaks with *d* spacing of 3.2 and 2.7 Å are attributed to the (004), (101) reflections of nanostructured 3R-MoS_2 (JCPDS 17–0744). The energy dispersive X-ray (EDX) data in Fig. 1*b* confirms that the nanowire has only Mo and S without any other impurities. The Al peaks are because of the substrate used for dispersing the samples, which indicate we have not mixed any impurity element in the preparation process. In

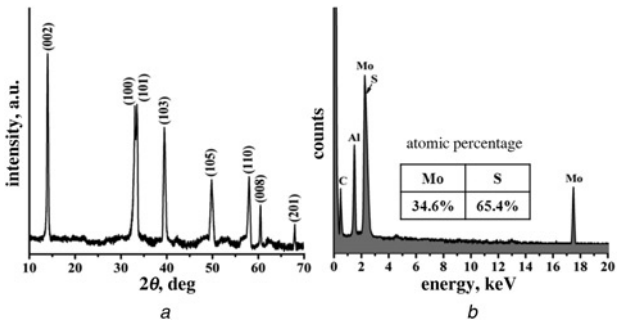

Figure 1 *XRD pattern of MoS_2 nanowires (Fig. 1a), and EDX spectrum of MoS_2 nanowires (Fig. 1b), inset of Fig. 1b shows S/Mo atomic ratios obtained by EDX*

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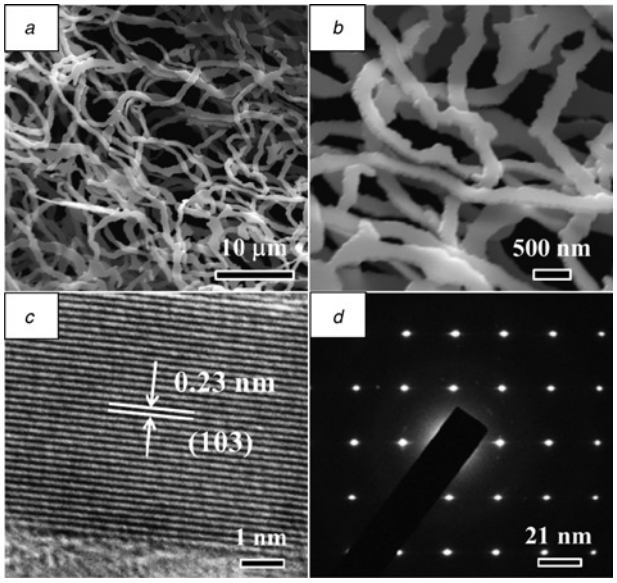

Figure 2 *Low-magnification (Fig. 2a) and high-magnification (Fig. 2b) SEM image of MoS_2 nanowires; HRTEM image of individual MoS_2 nanowires (Fig. 2c); SAED pattern of MoS_2 nanowires (Fig. 2d)*

addition, the inset to Fig. 1*b* shows S/Mo atomic ratios obtained by EDX. Since the S/Mo atomic ratios are 1.89, the nanowires are not completely sulphided, which is also observed in a previous report [30].

Figs. 2*a* and *b* show the SEM images of MoS_2 nanowires on adhesive tape. The size of the MoS_2 nanowires are about dozens of microns in length and 500 nm diameter. Fig. 2*c* is a high-resolution transmission electron microscope (HRTEM) image of the individual MoS_2 nanowires. The planes with interplanar spacing of 0.23 nm are corresponding to the (103) crystal faces. The corresponding selected area electron diffraction (SAED) pattern (Fig. 2*d*) indicates that the MoS_2 nanowires show an excellent single-crystalline structure.

The hysteresis loop (M–H) of MoS_2 nanowires with a magnetic field from −2 to 2 T at room temperature is shown in Fig. 3*a*. The single-crystalline MoS_2 nanowires show obvious ferromagnetism with coercivity about 200 Oe at room temperature (inset to Fig. 3*a*). The saturation magnetisation is about 1.1 emu/g. Fig. 3*c* shows that MoS_2 nanowires powder are strongly attracted by the permanent magnet. Therefore the MoS_2 nanowires show substantial ferromagnetism at room temperature. Ferromagnetism of the MoS_2 originating from the presence of zigzag Mo-edges and sulphur vacancies was predicted [25–28], where zigzag Mo-edges and sulphur vacancies can lead to strong ferromagnetism of several μ_B/atom.

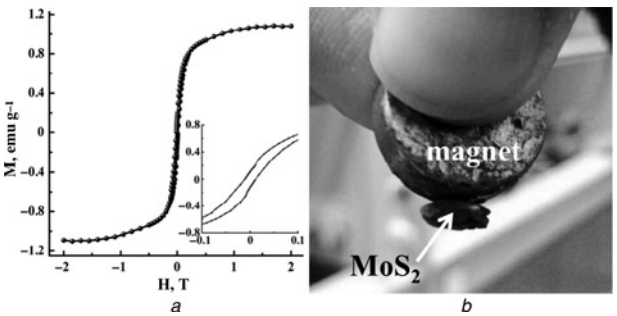

Figure 3 *M–H hysteresis loops for MoS_2 nanowires measured at room temperature (Fig. 3a), inset is magnification of one segment; real picture showing that the MoS_2 nanowires powder are strongly attracted by permanent magnet (Fig. 3b)*

The ferromagnetism observed in MoS_2 thin film and MoS_2 bulk at room temperature was attributed to the existence of the zigzag edges in the ferromagnetic ground state [29, 30]. The saturation magnetisation of MoS_2 thin film is 2.1 emu/g [29]. Here, the substantial ferromagnetism of the MoS_2 nanowire should originate from the presence of zigzag Mo-edges and sulphur vacancies because the MoS_2 nanowires are not completely sulphided because of the S/Mo atomic ratios 1.89.

4. Conclusion: In summary, single-crystalline MoS_2 nanowires were prepared by a hydrothermal method. HRTEM and SAED analysis show the nanowires present single-crystalline structures. The characterisation results of hysteresis loops (M–H) indicate that the single-crystalline nanowires present a substantial ferromagnetism at room temperatures. The substantial ferromagnetism of the MoS_2 nanowires should originate from the presence of zigzag Mo-edges and sulphur vacancies.

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6 References

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