

Magnetic MoS₂ Interface Monolayer on a CdS Nanowire by Cation Exchange

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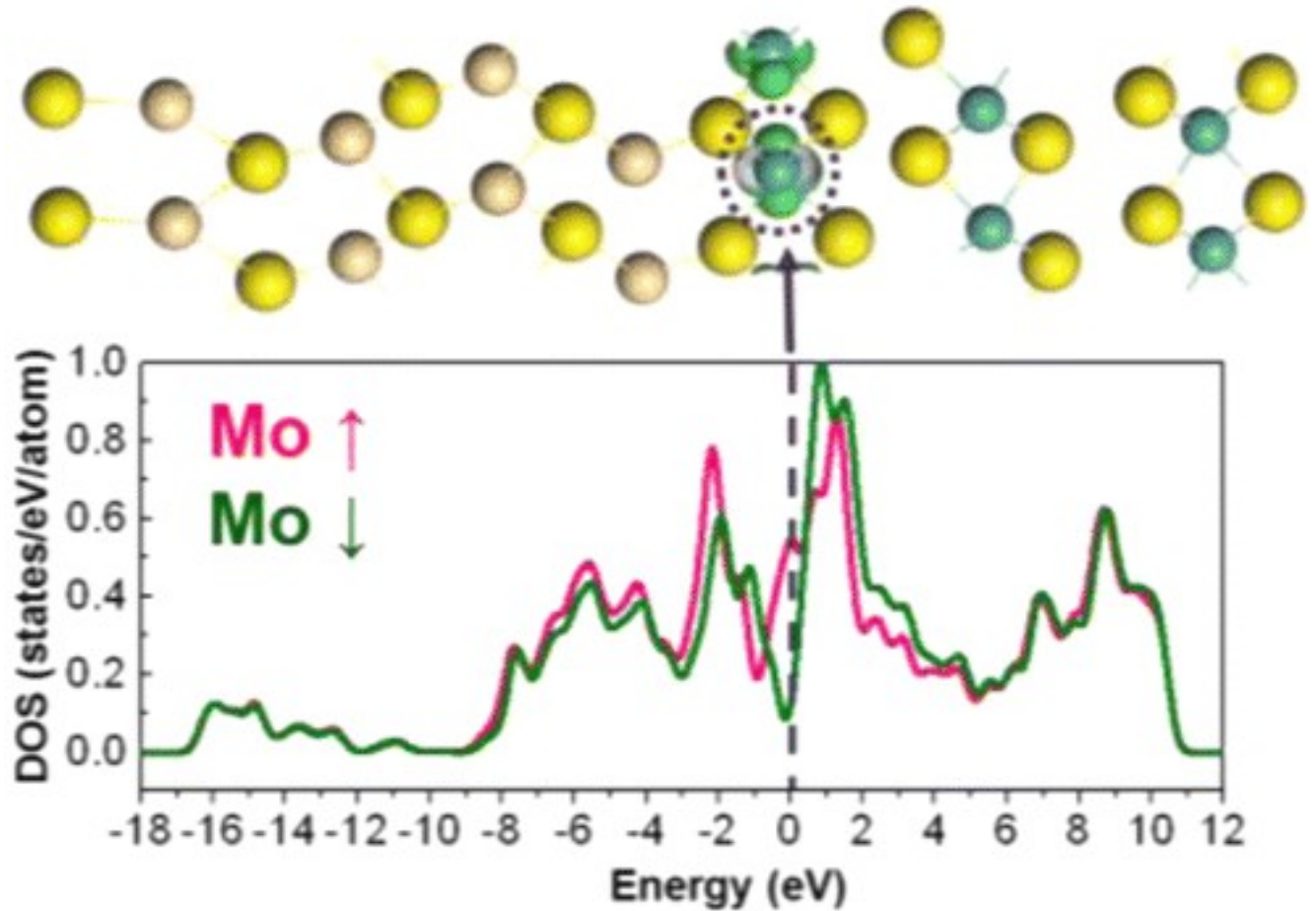
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Abstract



MoS₂ atomic layers have recently attracted much interest because of their two-dimensional structure as well as tunable optical, electrical, and mechanical properties for next-generation electronic and electro-optical devices. Here we have achieved facile fabrication of MoS₂ thin films on CdS nanowires by cation exchange in solution at room temperature and importantly observed their extraordinary magnetic properties. We establish the atomic structure of the MoS₂/CdS heterostructure by taking atomic images of the MoS₂/CdS interface as well as performing first-principles density functional geometry optimizations and scanning transmission electron microscopy annular dark field image simulations. Furthermore, our first-principles density functional calculations for the MoS₂/CdS heterostructure reveal that the magnetism in the MoS₂/CdS heterostructure stems from the ferromagnetic MoS₂ monolayer next to the MoS₂/CdS interface. The ferromagnetism is attributed to the partial occupation of the Mo $d_{x^2-y^2}/d_{xy}$ conduction band in the interfacial MoS₂ monolayer caused by the mixed covalent–ionic bonding among the MoS₂ and CdS monolayers near the MoS₂/CdS interface. These findings of the ferromagnetic MoS₂ monolayer with large spin polarization at the MoS₂/semiconductor interface suggest a new route for fabrication of the transition

metal dichalcogenide-based magnetic semiconductor multilayers for applications in spintronic devices.

Introduction

Transition metal dichalcogenide (TMD) monolayers,⁽¹⁻⁴⁾ especially those of molybdenum disulfide (MoS₂),⁽⁵⁻⁸⁾ have recently attracted much interest because of their controllable optical, electrical, and mechanical properties for next-generation devices. Bulk MoS₂ consists of sandwichlike S–Mo–S monolayers in which each Mo atom is connected to six S atoms with covalent bonds. The sandwich MoS₂ monolayers are bound together by weak van der Waals forces. The band structure of MoS₂ undergoes a remarkable change from an indirect band gap of ~1.2 eV in the bulk to a direct one of ~1.8 eV for a single monolayer.⁽⁹⁾ MoS₂ nanowires exhibit excellent electrochemical performance in lithium ion batteries.⁽¹⁰⁾ Recent researches have been focused on the excellent optical and electrical properties of MoS₂, and some are also related to the novel magnetic properties of MoS₂. For example, it has been reported that the valley magnetic moment of the MoS₂ monolayer could be electrically tuned⁽¹¹⁾ and that zigzag and armchair nanoribbons of MoS₂ could exhibit metallic (ferromagnetic) and semiconducting (nonmagnetic) behavior.⁽¹²⁻¹⁵⁾ It has also been predicted that large spin polarization could be induced in the interfacial MoS₂ monolayer in the ferromagnetic Fe₄N/MoS₂ bilayer because of the magnetic proximity effect.⁽¹⁶⁾ Spintronic devices are being developed with vigorous efforts,^(17, 18) and a spin transistor^(5, 19, 20) is believed to be the most promising next-generation spintronic device.

Although a large amount of research has been directed at the formation of MoS₂ films with atomic thickness, scarce attention has been paid to the process of formation of MoS₂ films and the bonding and physical properties of the MoS₂ layer with other semiconductor materials. Here we use cation exchange to grow epitaxial MoS₂ layers on the surface of CdS nanowires (NWs) at room temperature. Remarkably, we discover that the MoS₂/CdS heterostructures are ferromagnetic. Our first-principles density functional calculations reveal that the magnetism originates from the MoS₂ monolayer at the MoS₂/CdS interface with a spin magnetic moment of ~0.5 μ_B on the Mo atom and a large spin polarization (~63%) of the electronic states at the Fermi level. The occurrence of magnetization in the interfacial MoS₂ monolayer is attributed to the Mo cation sharing of its d electron with the Cd cation. As MoS₂ is considered to be an excellent material for transistors,⁽⁵⁾ the findings presented here of the itinerant magnetism in the MoS₂ monolayer at the MoS₂/semiconductor

interface may reveal a new opportunity for the fabrication of the magnetic two-dimensional (2D) TMD materials on three-dimensional (3D) nanostructures for application in spin transistors and other semiconductor spintronic devices.

Experimental and Computational Methods

CdS NW Synthesis

CdS NWs were grown by using the method reported in ref [21](#).

Cation Exchange Transformation

CdS NWs were dipped into ethylene glycol (99.5%, Sigma-Aldrich) containing 0.1 M molybdenum(V) chloride (Alfa Aesar, 99.6%) at room temperature. After 6 h, the CdS NWs completely transformed into MoS₂ NWs. We can change the MoS₂ shell thickness by varying the reaction time.

Instrumentation

FE-SEM images were obtained using a FEI Helios 1200+ FE-SEM instrument. TEM images were recorded using JEOL ARM200F and 2010F electron microscopes. Raman measurements were taken with a Horiba Jobin Yvon, LABRAM HR 800 UV instrument. The magnetic measurements were taken using a SQUID instrument (MPMS XL-7).

Scanning Transmission Electron Microscopy (STEM) Image Simulations

Scanning transmission electron microscopy annular dark field (STEM-ADF) image simulations of the model MoS₂/CdS heterostructures were performed with QSTEM.[\(22\)](#) The input parameters were set according to our experimental conditions, including the probe size, the convergence angle, and the acceptance angle of the ADF detector. To enhance the contrast of the sulfur atoms, the medium-range ADF mode was selected instead of the high-angle ADF mode by proper adjustment of the camera length. The detector angle is at a pivot condition (with 20–60 mrad) between the medium-range ADF mode and the high-angle ADF mode.

Density Functional Calculations

Several initial atomic models of the MoS₂/CdS heterostructure were constructed by different combinations of MoS₂ (00 $\bar{2}$) and CdS (002) thin layers. First-principles geometry optimizations for these initial atomic models of the MoS₂/CdS heterostructure were performed on the basis of density functional theory (DFT) with the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof form.[\(23\)](#) The optimized MoS₂/CdS heterostructure models were then used to simulate the STEM-ADF image. The atomic model that produces the image best fitting to the real STEM-ADF

image is displayed in [Figure 1](#), and also used in the subsequent GGA calculations of the electronic and magnetic properties of the MoS₂/CdS heterostructure. First-principles DFT-GGA calculations were performed by using the plane wave norm conserving pseudopotential method, as implemented in the Cambridge Serial Total Energy Package (CASTEP). The plane wave basis set cutoff energy is 720 eV. We used a fine k-point mesh of 5 × 8 × 1 for the Brillouin zone integration throughout.

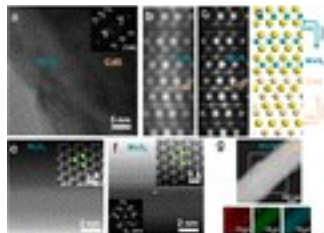


Figure 1. Heterojunction area analysis of MoS₂/CdS NWs after cation exchange. (a) High-resolution TEM image of the MoS₂/CdS heterostructure at the junction area (after reaction for 3 min). The inset is the corresponding FFT pattern. (b) STEM-ADF image of the MoS₂/CdS heterostructure (after reaction for 3 min). (c) Simulated STEM-ADF image of the MoS₂/CdS heterostructure. (d) Atomic model of the MoS₂/CdS junction. (e) STEM-ADF image of the MoS₂ region (after reaction for 3 min). The top right inset is the magnified image of panel e. (f) STEM-ABF image of the MoS₂ region (after reaction for 3 min). The top right and bottom left insets are the magnified image and FFT pattern, respectively. The blue and yellow dots represent Mo and S atoms, respectively. (g) STEM image and EDS mapping of CdS NW after Mo ion exchange for 10 min.

Results and Discussion

Cation exchange is an ionic reaction process for III–V and II–VI semiconductors and metal–organic frameworks for changing the components and structures⁽²⁴⁻²⁶⁾ as well as a convenient method for fabricating optical and electrical devices.⁽²⁷⁾ In a previous work, ion exchange was used to convert CdS nanowire templates to Cu₂S/Ag₂S superlattice p/n heterojunction NWs due to ionic bonding preferences between the different cation and anion.⁽²¹⁾ In the work presented here, MoS₂ layers were grown on CdS nanowires by cation exchange and the magnetic properties of MoS₂ (shell)/CdS (core) NWs were explored. CdS NWs were dipped in a molybdenum ionic solution at room temperature (RT), and atomic layers of MoS₂ were grown on CdS NWs. By control of the reaction time, different thicknesses, from one atomic layer to tens of atomic layers, of MoS₂ can be grown on CdS NW as a shell by cation exchange. Finally, the CdS NWs were completely transformed to MoS₂ NWs after several hours.

The ex situ Raman spectra of cation exchange from CdS NWs to MoS₂ NWs with different reaction times of up to 6 h were monitored. Via identification of the E_{2g}¹ (in-plane vibration) and A_{1g} (out of plane) peaks, the gradual formation of MoS₂ structure with increasing reaction time can be inferred ([Figure S1](#) and ref [28](#)). The data exhibit clearly the 302 cm⁻¹ peak, which is the first-order longitudinal optical mode (1LO) of CdS. After cation exchange, the CdS 1LO peak shifts gradually with strain and eventually disappears. On the other hand, the magnitudes of E_{2g}¹ and A_{1g} signals of MoS₂ increase gradually. It is difficult to identify the actual location of the E_{2g}¹ peak at 376 cm⁻¹ near the CdS peaks until the completion of the reaction. The A_{1g} peaks during the cation exchange from CdS to MoS₂ NWs are at 408 cm⁻¹ (2 min), 405 cm⁻¹ (3 min), 407 cm⁻¹ (4 min), 407 cm⁻¹ (5 min), 405 cm⁻¹ (10 min), 407 cm⁻¹ (30 min), 407 cm⁻¹ (1 h), 406 cm⁻¹ (2 h), and 406 cm⁻¹ (6 h). It indicates that the stress and strain are varied with reaction time and MoS₂ thickness. SEM images are shown in [Figure S2](#). Bright field transmission electron microscopy (BF-TEM) and scanning transmission electron microscopy–energy dispersive spectroscopy (STEM–EDS) were performed to obtain structural information about the MoS₂/CdS interface. We analyzed the MoS₂ on the CdS NW surface after cation exchange reaction for 3–10 min by BF-TEM ([Figure 1a](#)). After STEM imaging and EDS mapping of Mo, Cd, and S ([Figure 1g](#)), the core–shell structure of CdS–MoS₂ is evident. The scanning transmission electron microscopy annular dark field (STEM-ADF) image ([Figure 1b](#)) further reveals that MoS₂ (002̄) is connected with CdS (002) ([Figure 1b](#)). The STEM-ADF image matches rather well with the simulated image ([Figure 1c](#)) using the atomic model described below ([Figure 1d](#)). We built many atomic models for the MoS₂/CdS heterostructure and then performed first-principles geometry optimization calculations for these models that were used in the STEM-ADF image simulations by QSTEM.[\(22\)](#) The MoS₂/CdS heterostructure shown in [Figure 1d](#) is the heterostructure model with the simulated STEM-ADF image ([Figure 1c](#)) fitted best to the real STEM-ADF image ([Figure 1b](#)). From the STEM-ADF ([Figure 1e](#)) and ABF ([Figure 1f](#)) images, with magnified images as insets, the hexagonal structure of MoS₂ along the [001] direction is evident. Both CdS and MoS₂ are of a hexagonal closely packed (hcp) crystal structure with different lattice parameters. For CdS, $a = b = 0.413$ nm and $c = 0.671$ nm. For MoS₂, $a = b = 0.316$ nm and $c = 1.229$ nm. Consequently, for growth of (002̄) MoS₂ on (002) CdS, the lattice mismatch between CdS and MoS₂ would be as high as 23%. On the other hand, no dislocations were observed at the interface. The absence of misfit dislocations is attributed to the difficulty in nucleation of dislocations in nanostructures.[\(29, 30\)](#)

The hysteresis loops of CdS NWs and MoS₂/CdS NWs have been obtained by a superconducting quantum interference device (SQUID) ([Figure 2a–c](#) and [Figure S2](#)) with different cation exchange

time (3 s, 6 s, 9 s, 12 s, 1 min, 5 min, 10 min, 30 min, 60 min, 2 h, and 6 h). After cation exchange for 6 h, CdS NWs ($M_s = 1.135 \times 10^{-3}$ emu/g, and $H_{c\perp} = 215.8$ Oe) transform completely to MoS₂NWs ($M_s = 5.53 \times 10^{-3}$ emu/g, and $H_{c\perp} = 149.9$ Oe), and both of them are ferromagnetic. Obviously, growth for 1 min of MoS₂ on CdS NWs leads to the strongest saturation magnetization intensity. In addition, the low-temperature ($T = 4$ K) hysteresis loop shows a coercivity ($H_{c\perp} = 973$ Oe) and saturation magnetization intensity ($M_s = 4.43 \times 10^{-2}$ emu/g) (Figure S3) higher than the coercivity ($H_{c\perp} = 200$ Oe) and saturation magnetization intensity ($M_s = 1.3 \times 10^{-2}$ emu/g) at room temperature. Figure 2d reveals that the M_s decreases with MoS₂ thickness.

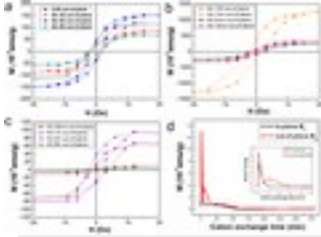


Figure 2. Magnetic measurements of MoS₂/CdS NWs. (a–c) Hysteresis loops of CdS NWs and MoS₂/CdS NWs in the out-of-plane direction. M is magnetization, and H is applied field. (d) Saturation magnetization of MoS₂/CdS NWs as a function of cation exchange time.

For further exploration of the origin and nature of the observed magnetization (M), the knowledge of the electronic structure and atom-resolved magnetization in the MoS₂/CdS heterostructure is essential. Therefore, we have performed self-consistent spin-polarized electronic structure calculations within the DFT-GGA.⁽²³⁾ The atomic model shown in Figure 1d, which generates the simulated STEM-ADF image (Figure 1c) that fits best to the real STEM ADF image (Figure 1b), has been used in the DFT-GGA calculation.

A previous DFT-GGA calculation shows that free-standing few-layer thin films of MoS₂ have no magnetic moment.⁽³¹⁾ In contrast, this calculation shows that the MoS₂ monolayer next to the CdS substrate becomes ferromagnetic with a Mo magnetic moment (m_s) of $\sim 0.5 \mu_B$ and a large electronic state spin polarization (P) of $\sim 63\%$ at the Fermi level (Figure 3d). Spin polarization $P = (N_{\uparrow} - N_{\downarrow}) / (N_{\uparrow} + N_{\downarrow})$, where N_{\uparrow} and N_{\downarrow} are the spin-up and spin-down densities of states (DOSs) at the Fermi level (EF), respectively. The Mo magnetic moment and spin polarization are greatly reduced in the second ($m_s = 0.01 \mu_B$, and $P = 15\%$) and third ($m_s = 0.00 \mu_B$, and $P = 2\%$) monolayers of MoS₂ away from the interface, as demonstrated by the calculated Mo-decomposed spin-resolved densities of states (DOSs) displayed in Figure 3d (and also Figure S5). Experimentally, the thinner MoS₂ layers are observed to possess a higher magnetization (M_s), and this is consistent with the results of the

DFT calculation. Clearly, both experimental data and DFT calculation indicate that the interfacial MoS₂ layer has the predominant contribution to the MoS₂/CdS magnetic properties.

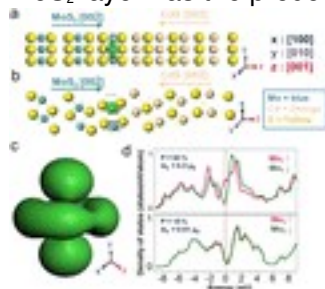


Figure 3. Atomic structure and DFT calculation of the magnetic property of the MoS₂/CdS heterostructure. Atomic models of the MoS₂/CdS heterostructure with MoS₂ (002) connecting with CdS (002) along (a) [010] and (b) [110] zone axes. The calculated spin density is concentrated at the first layer of Mo atoms from the junction. (c) Shape (isosurface) of the spin density of the Mo atom on the interfacial MoS₂ monolayer. (d) Spin-resolved DOSs of the Mo atoms on the first and second layers of the interface (top and bottom panels). The red dashed line indicates the Fermi level.

The observed dependence of magnetization on the thickness of the MoS₂ layer on the CdS NW is consistent with the theoretical finding of the magnetism in the MoS₂ monolayer at the MoS₂/CdS interface as revealed by our atomic model (Figures 1d and 3a). Raman peaks (E_{2g}^1 and A_{1g}) of the MoS₂ layer (Figure S1) are clearly seen after cation exchange for 2 min, indicating that the quality of the MoS₂ structure improves as the thickness increases. Indeed, our Raman results show that our MoS₂ layer has a fine 2D structure on the CdS NW with clear in-plane and out-of-plane vibration modes. This explains that the few-layer thick MoS₂ structures have a poor magnetic property. For example, for very few-layer thick MoS₂ films on CdS NWs [3 s (0.5 layer), 6 s (1 layer), 9 s (1.5 layers), and 12 s (2 layers)], the M_s values are lower than that for 5 nm (reaction for 5 min) thick MoS₂ on CdS NWs. For MoS₂ with an improved structure, the interfacial magnetism starts to dominate the magnetic properties. On the other hand, for MoS₂ shells of >5 nm on CdS NWs, the influence of the interfacial magnetism is weakened. As a result, the magnetization decreases with an increase in MoS₂ thickness. Overall, as the CdS NW gradually transforms to the MoS₂ NW, the maximal magnetization moment (M_{max} or M_s) increases first sharply with the formation of a thin shell of MoS₂ and then decreases rapidly. This phenomenon is similar to the variation of the photoluminescence intensity of MoS₂ with thickness.⁽³²⁾ Furthermore, the magnetic force microscopy (MFM) data also show that the magnetic property of MoS₂ depends on the number of layers.⁽³³⁾ The calculated spin density distribution in the MoS₂/CdS heterostructure is exhibited in panels a and b of Figure 3, and that of the Mo atom in the interfacial MoS₂ monolayer is displayed in Figure 3c.

Clearly, there is significant spin density only in the interfacial MoS₂ monolayer ([Figure 3a,b](#)), where the spin density distribution of Mo is similar to that of the d_{x²-y²} orbital ([Figure 3c](#)). The results indicate that the major contribution comes from Mo d orbitals. This is because the Fermi level is raised above the bottom of the conduction Mo d_{x²-y²} and d_{xy} bands in the interfacial monolayer, as revealed by calculated Mo-decomposed spin-resolved DOSs shown in [Figure 3d](#) (see also [Figure S5](#)). Interestingly, the calculated spin-resolved DOS curves show that the local DOS of the Cd atoms on the interfacial Cd monolayer is also spin-polarized ([Figure S6](#)), because of the magnetic proximity effect on the Cd atoms by the magnetic Mo atoms via the S atoms across the interface. For example, the spin polarizations for the S atoms on the interface S monolayer and the Cd atoms on the Cd monolayer next to the interface are 20% (S_{M1}) and 16% (Cd₁), respectively (see [Figure 4b](#) and also [Figures S6 and S7](#)).

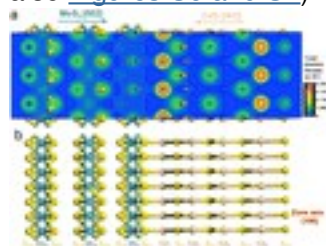


Figure 4. Electron density distribution of the MoS₂/CdS heterostructure. (a) Total electron density distribution of the MoS₂/CdS heterostructure shown with the isosurface (blue line, isovalue of 0.13876 e/Å³). (b) Atomic model of the MoS₂/CdS heterostructure with the [100] zone axis.

[Figure 4a](#) shows the calculated charge density distribution in the MoS₂/CdS heterostructure as modeled by the atomic model shown in [Figure 3b](#). For the sake of discussion, the different atomic locations in the vicinity of the MoS₂/CdS interface are labeled, as shown in [Figure 4b](#). The charge density distribution in the region from the S_{M4} to Cd₂ atom layer is rather flat, having a similar isosurface with an isovalue of 0.139 e/Å³. Inside the region, the electron density in some areas is higher than the isovalue, indicating some bonding between the S and Cd atoms across the MoS₂/CdS interface. This covalent bonding could be attributed to the similar electronegativities of the Mo (1.3) and Cd (1.5) atoms. Remarkably, the calculated DOS curves ([Figure S5](#)) show that this covalent bonding causes some charge transfer from the Mo d bands in the outer MoS₂ monolayer (Mo₃) to the Mo d bands in the interfacial MoS₂ monolayer (Mo₁), leading to the partial occupation of the Mo d_{x²-y²} and d_{xy} dominant bands of the Mo₁ atoms. This charge transfer is also seen from the calculated numbers of valence electrons on the Mo₁ (6.38), Mo₂ (6.17), and Mo₃ (6.02) atoms ([Table S1](#)). As a result, the strong exchange interaction among the Mo d electrons then gives rise to the

formation of the Mo₁ spin magnetic moment, and hence the ferromagnetic MoS₂ monolayer next to the MoS₂/CdS interface.

Conclusions

In summary, magnetic MoS₂ thin films have been grown on CdS NWs by cation exchange at room temperature. The magnetism in the MoS₂/CdS heterostructure was shown to stem from the ferromagnetic MoS₂ monolayer next to the MoS₂/CdS interface by first-principles DFT-GGA calculations. The ferromagnetism was attributed to the partial occupation of the Mo d_{x²-y²}/d_{xy} conduction band in the interfacial MoS₂ monolayer caused by the mixed covalent–ionic bonding among the MoS₂ and CdS monolayers near the MoS₂/CdS interface. This work thus offers a new paradigm for fabrication of the transition metal dichalcogenide-based magnetic semiconductor multilayers for applications in spintronic devices such as tunnel junctions with high magnetoresistance.

Supporting Information

The Supporting Information is available free of charge on the [ACS Publications website](https://pubs.acs.org) at DOI: [10.1021/acs.jpcc.6b07679](https://doi.org/10.1021/acs.jpcc.6b07679).

- Additional figures displaying measured Raman spectra, SEM images and hysteresis loops, and calculated atom- and orbital-decomposed densities of states and additional tables listing calculated occupation numbers of atomic orbitals and structural parameters of the atomic model adopted in the SEM image simulations and DFT-GGA calculations ([PDF](#))
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The authors declare no competing financial interest.

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