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Polarization-dependent optical absorption of MoS₂ for refractive index sensing

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As a noncentrosymmetric crystal with spin-polarized band structure, MoS₂ nanomaterials have attracts increasing attention in many areas such as lithium ion batteries, flexible electronic devices, photoluminescence and valleytronics. The investigation of MoS₂ is mainly focused on the electronics and spintronics instead of optics, which restrict its applications as key elements of photonics. In this work, we demonstrate the first observation of the polarization-dependent optical absorption of the MoS₂ thin film, which is integrated onto an optical waveguide device. With this feature, a novel optical sensor combining MoS₂ thin-film and a microfluidic structure has been constituted to achieve the sensitive monitoring of refractive index. Our work indicates the MoS₂ thin film as a complementary material to graphene for the optical polarizer in the visible light range, and explores a new application direction of MoS₂ nanomaterials for the construction of photonic circuits.

The discovery of novel functionalities of two dimensional (2D) nanomaterials or atomic membranes has attracted remarkable attentions^{1–4}, ever since the first demonstration of intriguing electrical and optical properties in isolated graphene^{5–12}. Most 2D atomic membranes could be obtained by the exfoliation of their bulk materials consisted by strongly bonded layers with weak interlayer interaction¹³. As the monolayer counterpart of the bulk material, these 2D nanomaterials enable a number of unique layer-dependent properties. Separated by forms of monolayers, the 2D atomic membranes include graphene and transition metal dichalcogenides (TMDCs)^{14–17}. For TMDCs, the ultrathin layer has a sandwich structure with the chalcogen atoms in two hexagonal planes separated by a plane of metal atoms. Compared with graphene, TMDCs offer complementary properties, which have both scientific and engineering interests. For example, the absence of a direct bandgap of graphene leads to low on/off switching ratios of field-effect transistors made of graphene. However, many TMDCs have sizable bandgaps indicating better candidates for new optoelectronic devices^{18,19}.

The 2D nanomaterial, MoS₂ (molybdenum disulfide) membrane, as a kind of TMDC semiconductor, has two hexagonal planes of S atoms coordinated through ionic-covalent interactions with the Mo atoms in a trigonal prismatic arrangement. It has distinctive electronic, optical, and catalytic properties with the geometry of the ultrathin layer, indicating intriguing applications for electronic and optical devices^{20–27}. Different from the centrosymmetric of graphene, the MoS₂ has non-inversion symmetry of the structure, which leads to a very strong spin coupling and valley confinement. For further understanding of the valley property of the MoS₂, the dynamic conductivity of the MoS₂ film was theoretically discussed based on a simplified Hamiltonian²⁸. According to the dynamic conductivity analysis, excess populations of a selected valley could be quantitative described¹⁹. In addition, it also demonstrates that there is the positive value of the imaginary part of the dynamic conductivity of MoS₂ in the visible region, which is opposite to the feature of graphene with the negative one. As reported in Ref. 28, the negative value of imaginary part induces the polarization-dependent absorption of graphene. With surface-coated on a fiber, graphene offers selective absorption of light only along vertical polarization (i.e., corresponding to transverse-magnetic (TM) mode of fiber), does not affect the light propagation with horizontal polarization (i.e., corresponding to transverse-electrical (TE) mode of waveguide)¹¹. This feature enables graphene based fiber operating as a broadband polarizer. It is reasonable to expect an analogues property of the MoS₂ membranes. In this work, we report the polarization-sensitive absorption of the MoS₂ membrane. The essence of the polarization-sensitive absorption is briefly discussed by the nature of electromagnetic modes in 2D nanomaterial combined with the analysis of the dynamic conductivity of the MoS₂. This observation of the novel optical property of TMDCs suggests potential applications for sensing. A novel refractive index detector is therefore designed and implemented for sensitive refractive index change within the range between 1 ~ 1.52.

Figure 1 | Experimental setup for the MoS₂ absorption. (a) A schematic illumination of the MoS₂ absorption measurement. (b) Morphological image of MoS₂ film by the atomic force microscope. Scratches are made intentional for the measurement of thickness. The thickness of MoS₂ on the white line is plotted in (c). (d) Raman spectrum of MoS₂ film. Polarized optical images of the scattered light from the waveguide with the TE (e) and TM (f) polarization, respectively.

Results

A MoS₂ film was coated on to the surface of the planar Nd:YAG (neodymium doped yttrium aluminum garnet) waveguide structure in order to investigate the polarization dependent absorption of MoS₂ membrane. Since the light propagates in the planar waveguide layer, an evanescent field of the mode exists near the waveguide surface, enabling the interaction of the MoS₂ and light wave. We tested the polarization dependent absorption of the MoS₂ film, which was detected by coupling light with different polarizations into waveguide. The waveguide was fabricated by the ion implantation on the surface of Nd:YAG crystal. Fig. 1a shows the schematic plot of the above measurement.

Figure 1b depicts the morphological image of the MoS₂ thin film taken by the Scanning Probe Microscope (Dimension Icon, Veeco Instruments Inc.). Obviously, the MoS₂ film presents a hierarchical

structure and has the maximum thickness of 6.486 nm (Fig. 1c). Considering the thickness of the monolayer MoS₂ (0.6 nm ~ 0.7 nm)²⁹, the number of the MoS₂ layers was determined to be 9 ~ 11. Figure 1d shows representative Raman spectra for the MoS₂ film. We observed E and A modes near 384 and 407 cm⁻¹, respectively. These data indicates that multi-layer MoS₂ was well deposited onto the waveguide surface²⁹.

To obtain a clear effect for the absorption of MoS₂ film, we detected the power variation of the scattered light from the waveguide structure with the experimental setup in Fig. 1a, utilizing a solid state laser operating at 532 nm as the light source. As the light propagating in the waveguide will be scattered by the color center or defects generated by the ion beam irradiation process. And the power of the scattered light is proportional to the intensity of the

Figure 2 | Polarization dependent absorption of MoS₂. The polar image of the output light power from the waveguide along with the polarization variation of the detecting light. The wavelength of the detecting light was 532 (green dots), and 1064 nm (pink squares), respectively.

propagation light. Hence, the power variation of the scattered light along the propagation direction leads to a technique to modulate the variation of the light intensity in the waveguide³⁰.

As shown in Figs. 1e and 1f, the gradually diminishing scattered light from waveguide (bright green lines) can be clearly observed even by the naked eye. For the TE polarization, a short diminishing line was depicted in Fig. 1e, indicating a quick absorption by the MoS₂ film. And the intensity of the light with the polarization of TM was slightly changed along the propagation distance. By comparing Fig. 1e and 1f, one can conclude that there was a polarization dependent absorption of MoS₂.

To further confirm this phenomenon, we modulate the polarization of the input light (0 dB m) under the same coupling condition and plotted the all-angle power variation of the output light in Fig. 2a. With the propagation distance of 10 mm, the minimum output power was −3.4 dB m at TE polarization corresponding to maximum of −0.4 dB m at TM polarization. The essence of this polarization dependent absorption could be demonstrated by the nature of electromagnetic modes in 2D materials. In the 2D layer, the electromagnetic modes propagating could be described by the equations below³¹:

For TM waves

$$1 + \frac{2\pi i \sigma(\omega) \sqrt{q^2 - \omega^2/c^2}}{\omega} = 0 \quad (1)$$

For TE waves

$$1 - \frac{2\pi i \sigma(\omega)}{\omega \sqrt{q^2 - \omega^2/c^2}} = 0 \quad (2)$$

where $\sigma(\omega)$ is the local dynamic conductivity of the 2D gas and c is the velocity of light. It could be concluded from Eqs. (1) and (2) that the absorption of waves are decided by the imaginary part of the conductivity. With the negative (positive) imaginary part of $\sigma(\omega)$, only the TE (TM) mode can propagate in such structures and the TM (TE) mode is forbidden in the 2D electronic layer. As demonstrate in Ref. 28, the MoS₂ film has the positive imaginary part of the conductivity within the visible range. Hence there is the possibility of a stronger absorption of TE light compared with TM, which has a good coherence of the experiment results.

We also measured the polarization dependent absorption of MoS₂ at near-infrared wavelength (1064 nm) with the waveguide structure. As shown in Fig. 2b, little absorption was observed for the wavelength of 1064 nm. And there was indifferent absorption with

polarization different from the green light in Fig. 2a. The origin of the absorption variation with the wavelength could be attributed to the electronic structure of MoS₂. For the multilayer MoS₂, the value of the indirect gap was over 1.20 eV corresponding to the little absorption in the near-infrared range²³. So there is hard to observe the optical absorption at the wavelength of 1064 nm.

By changing the thickness of the MoS₂ film from ~1.9 nm to ~39 nm, we compared the absorption variation of the MoS₂ film with multi-layers. As illuminated in Fig. 3a, there is a gradually accumulate absorption along with the increasing of the thickness, which was finally stable at 4.93 dB with the thickness more than 27 nm. As demonstrated in Fig. 3b, the interaction of light with the MoS₂ film depended on the overlapping of the evanescent field and the MoS₂ film. The absorption ratio of the MoS₂ is supposed to be proportional to the intensity of the light in MoS₂ described by the equation below:

$$I_{abs} = C I_{MoS_2} \quad (3)$$

where C is a parameter decided by the thickness of MoS₂ film, I_{abs} is the power absorbed by MoS₂ film and I_{MoS_2} is the power of the evanescent field overlapped with MoS₂ film. According to the reconstructed refractive index distribution of the waveguide, we calculated the evanescent field of waveguide with different thickness of MoS₂.

Figure 3b shows the refractive index distribution of the waveguide structure with a typical “enhanced well + optical barrier” shape³², which is one of the typical profiles for ion implanted waveguides. As one can see, an enhanced index well with $\Delta n \approx +0.003$ near the surface was constructed after the ion implantation, and at the same time, there is an optical barrier with the reduced refractive index ($\Delta n \approx -0.002$) at the depth of 3 μm . The light was confined in the sandwich waveguide structure which consists of the optical barrier, enhanced well and air. Based on this refractive index distribution, the propagation mode at 532 nm was calculated by the beam propagation method (BPM) in Fig. 3c. The inset shows the evanescent field near the surface overlapping with the MoS₂ film. The variation of the evanescent field intensity in the MoS₂ along with the thickness was shown in Fig. 3a, which it has a similar variation tendency with the power of the absorbed light (the power of input light was 0 dB m).

Discussion

We demonstrate the polarization dependent absorption of MoS₂ film. Through the interaction of an electromagnetic field with

Figure 3 | Absorption extinction ratio vs. MoS₂ thickness. (a) Polarization extinction ratio (red labels), calculated relative light intensity in MoS₂ film (blue solid line) and measured absorbed light power (red square) as a function of the thickness of MoS₂ film. (b) The refractive index distribution of the waveguide structure. (c) The shape of the propagation mode in the waveguide at the wavelength of 532 nm. The inset diagram shows the evanescent field near the surface. (d) A schematic illustrates the interaction of the evanescent-field and the MoS₂ film. The inset shows the overlap of the evanescent field and the MoS₂ film with the thickness of 100 nm.

MoS₂ film, there is an extinction ratio (propagation loss of the waveguide induced by MoS₂ absorption) up to 4.9 dB/cm in the visible band for the light with TE. This behavior is similar to the graphene. However, there are some significant differences. At first, the MoS₂ film has the extinction ratio with TE instead of TM polarized light. In this manner, the MoS₂ could be used as a complementary material to graphene. Second, this property is only available in the visible light region. Besides, it is proved the absorption of MoS₂ film is sensitive to the overlapping of the evanescent field and the MoS₂, which provides a possibility for the design of a novel optical environment-sensitive sensor.

For example, we have presented a novel refractive index measuring system for the liquid using MoS₂ as optical sensors based on the polarization dependent absorption property of MoS₂ film as depicted in Fig. 4a. The microfluidic channel was filled with the liquid, such as water ($n \approx 1.33$), alcohol ($n \approx 1.35$), or immersion oil ($n \approx 1.48$ or 1.52). Due to the disturbance of the refractive index of the liquid, the shape of the evanescent field was modified and the intensity of light in the MoS₂ region was changed as shown in Fig. 4b. The variation of the absorbed power along with the refractive index of liquid was shown in Fig. 4c, which displayed an exponential trend. There was a sharp variation ratio of absorbed power within the range of $1.33 \sim 1.52$. Meanwhile a gradual variation for the refractive index was less than 1.33.

Similar to the discussion for Fig. 3a, the variation of the MoS₂ absorption was proportional to the intensity of the light in MoS₂. With different liquid in microfluidic channel, the extinction ratio was measured and shown in Fig. 4c. It has an exponential decrease form

with the refractive index increasing, which is similar to the variation of the intensity change in MoS₂.

Methods

Fabrication of the waveguide. The waveguide used in this work was fabricated by the ion irradiation of a Nd:YAG crystal. The crystal was cut into dimensions of $10 \times 10 \times 2$ mm³ and optically polished. The carbon (C³⁺) ions at energy of 6 MeV were implanted onto a 10×2 mm² surface at the influence of 1×10^{15} ions/cm² by using a 2×1.7 MV tandem accelerator at Peking University, China. The ion beam was tilted by 7° off the normal plane to avoid channeling effect. With such a processing, a planar waveguide layer with a thickness of ~ 3 μm was constructed on the surface of Nd:YAG crystal.

Fabrication of microfluidic channel. The microfluidic channel was fabricated based on fused silica with the dimension of $10 \times 10 \times 2$ mm³. The biggest facets were optically polished. Two microfluidic channels with size of $5 \times 2 \times 0.5$ mm³ was produced by the chemical etching. Two holes with diameter of 0.5 mm were made on the bottom of each microfluidic channels as inlet and outlet.

Strategy for Sensor design. The strategy for this design consisted of a MoS₂ layer sandwiched between a waveguide structure and the liquid. A MoS₂ film with the thickness of 6.5 nm was coated onto the planar waveguide and a microfluidic channel sandwich structure was formed by bonding a microfluidic channel to the MoS₂ film. A 532 nm continuous wave laser was used as a light source. Using a half-wave plate, the light was adjusted to the circular polarization and coupled into the waveguide structure. Through a Glan-Taylor polarizer, the output light from the waveguide was splitted into two beams for the TE and TM polarizations, respectively. And the extinction absorption ratio change of the MoS₂ film was measured.

Refractive index distribution of YAG waveguide. The dark-mode spectrum of the planar waveguide was measured by a prism coupler (Model 2010, Metricon, USA). Based on the measured dark modes, the refractive index profile of the waveguide is reconstructed by the reflectivity calculation method (RCM)³³.

Figure 4 | Refractive index sensor (a) A design for the refractive index variation detector. (b) Calculated evanescent field corresponding to different kinds of liquid in the microfluidic channel. (c) The measured variation of absorbed light power (red circle) and simulated light intensity (blue circle with crossing) in MoS₂ film according to the refractive index of the coating film.

Measurement of waveguide propagation loss. The propagation losses (α_{wa}) of the waveguide structure were measured by the back-reflection method³⁰. The original propagation loss was measured to be 0.8 dB/cm and 0.5 dB/cm for TE and TM polarizations, respectively. In order to simplify the discussion, the loss generated by the waveguide structure was normalized in Section Results.

Measurement of polarization-dependent absorption. The experimental schematic of MoS₂-waveguide absorption was shown in Fig. 1a. Through a microscope objective ($\times 40$), the detecting light was coupled into the planar waveguide by the end-coupling method with a coupling efficiency of $\sim 10\%$. And the output light from the waveguide structure was collected by a long-work distance microscope objective. Through the comparison of the input and output light power (I_{in} and I_{out}), the loss induced by MoS₂ absorption (α_{MoS_2}) was calculated by the equation below:

$$\alpha_{MoS_2} = 4.34 \ln \frac{I_{out}}{I_{in}} - \alpha_{wa} \quad (4)$$

Deposition and characterization of MoS₂ film. The MoS₂ film was fabricated by the pulsed laser deposition (PLD) with polycrystalline MoS₂ as the starting material. A KrF excimer laser (Compex Pro 201, Coherent Inc.), which generated 20-ns laser pulses at wavelength of 248 nm, was employed for radiating and ablating the target material. The repetition rate and energy of the pulse laser for deposition were 5 Hz and 600 mJ, respectively. To enhance the uniformity of the MoS₂ film, both of the target and substrate were rotated and heated to 300°C during the deposition process. The topography of the MoS₂ film was imaged by a scanning probe microscope (Dimension Icon, Veeco Instruments Inc.). The Raman spectroscopy investigation was performed by a confocal laser scanning microscope.

- Wang, Q. H., Kalantar-Zadeh, K., Kis, A., Coleman, J. N. & Strano, M. S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nat. Nanotech.* **7**, 699–712 (2012).
- Neto, A. H. C. & Novoselov, K. New directions in science and technology: two-dimensional crystals. *Rep. Prog. Phys.* **74**, 082501 (2011).

- Lu, J. *et al.* Order-disorder transition in a two-dimensional boron-carbon-nitride alloy. *Nat. Commun.* **4**, 2681 (2013).
- Chen, Y. *et al.* Self-assembled topological insulator: Bi₂Se₃ membrane as a passive Q-switcher in an erbium-doped fiber laser. *J. Lightwave Technol.* **31**, 2857–2863 (2013).
- Novoselov, K. S. *et al.* A roadmap for graphene. *Nature* **490**, 192–200 (2012).
- Novoselov, K. S. *et al.* Electric field effect in atomically thin carbon films. *Science* **306**, 666–669 (2004).
- Bonaccorso, F., Sun, Z., Hasan, T. & Ferrari, A. C. Graphene photonics and optoelectronics. *Nat. Photon.* **4**, 611–622 (2010).
- Balandin, A. A. *et al.* Superior thermal conductivity of single-layer graphene. *Nano Lett.* **8**, 902–907 (2008).
- Mayorov, A. S. *et al.* Micrometer-scale ballistic transport in encapsulated graphene at room temperature. *Nano Lett.* **11**, 2396–2399 (2011).
- Bunch, J. S. *et al.* Impermeable atomic membranes from graphene sheets. *Nano Lett.* **8**, 2458–2462 (2008).
- Bao, Q. *et al.* Broadband graphene polarizer. *Nat. Photon.* **5**, 411–415 (2011).
- Zhang, H. *et al.* Z-scan measurement of the nonlinear refractive index of graphene. *Opt. Lett.* **37**, 1856–1858 (2012).
- Chhowalla, M. *et al.* The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat. Chem.* **5**, 263–275 (2013).
- Mattheis, L. F. Band structures of transition-metal-dichalcogenide layer compounds. *Phys. Rev. B* **8**, 3719–3740 (1973).
- Wilson, J. A. & Yoffe, A. D. Transition metal dichalcogenides: discussion and interpretation of observed optical, electrical and structural properties. *Adv. Phys.* **18**, 193–335 (1969).
- Mann, J. *et al.* 2-Dimensional Transition Metal Dichalcogenides with Tunable Direct Band Gaps: MoS₂(1-x)Se_{2x} Monolayers. *Adv. Mater.* **26**, 1399–1404 (2014).
- Komsa, H. *et al.* Two-Dimensional Transition Metal Dichalcogenides under Electron Irradiation: Defect Production and Doping. *Phys. Rev. Lett.* **109**, 035503 (2012).
- Yoffe, A. D. Layer compounds. *Annu. Rev. Mater. Sci.* **3**, 147–170 (1993).
- Mak, K. F., Keliang, H., Jie, S. & Heinz, T. F. Control of valley polarization in monolayer MoS₂ by optical helicity. *Nat. Nanotech.* **7**, 494–498 (2012).

20. Splendiani, A. *et al.* Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **10**, 1271–1275 (2010).
21. Kan, M. *et al.* Structures and Phase Transition of a MoS₂ Monolayer. *Phys. Chem. C* **118**, 1515–1522 (2014).
22. Bertolazzi, S., Brivio, J. & Kis, A. Stretching and Breaking of Ultrathin MoS₂. *ACS Nano* **5**, 9703–9709 (2011).
23. Mak, K. F. *et al.* Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **105**, 136805 (2010).
24. Splendiani, A. *et al.* Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **10**, 1271 (2010).
25. Radisavljevic, B. *et al.* Single-layer MoS₂ transistors. *Nat. Nanotech.* **6**, 147 (2011).
26. Yin, X. *et al.* Edge Nonlinear Optics on a MoS₂ Atomic Monolayer. *Science* **344**, 488 (2014).
27. Wang, Sh. *et al.* Broadband Few-Layer MoS₂ Saturable Absorbers. *Adv. Mater.* **26**, 3538 (2014).
28. Li, Z. & Carbotte, J. P. Longitudinal and spin-valley Hall optical conductivity in single layer MoS₂. *Phys. Rev. B* **86**, 205425 (2012).
29. Lee, C. *et al.* Anomalous lattice vibrations of single- and few-layer MoS₂. *ACS Nano* **4**, 2695–2700 (2010).
30. Ramponi, R., Osellame, R. & Marangoni, M. Two straightforward methods for the measurement of optical losses in planar waveguides. *Rev. Sci. Instrum.* **73**, 1117–1120 (2002).
31. Mikhailov, S. & Ziegler, K. New electromagnetic mode in graphene. *Phys. Rev. Lett.* **99**, 016803 (2007).
32. Chen, F. Micro- and submicrometric waveguiding structures in optical crystals produced by ion beams for photonic applications. *Laser Photonics Rev.* **6**, 622–640 (2012).
33. Chandler, P. J. & Lama, F. L. A New Approach to the Determination of Planar Waveguide Profiles by Means of a Non-stationary Mode Index Calculation. *Opt. Acta* **33**, 127 (1986).

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Author contributions

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Additional information

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