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 attracted 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 restricts 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 attentions1–11, ever since the first demonstration of intriguing electrical and optical properties in isolated graphene5–12. 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 devices18,19.

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 devices20–27. 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.
Results

A MoS$_2$ 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 MoS$_2$ 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 MoS$_2$ and light wave. We tested the polarization dependent absorption of the MoS$_2$ 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 MoS$_2$ thin film taken by the Scanning Probe Microscope (Dimension Icon, Veeco Instruments Inc.). Obviously, the MoS$_2$ film presents a hierarchical structure and has the maximum thickness of 6.486 nm (Fig. 1c). Considering the thickness of the monolayer MoS$_2$ (0.6 nm ~ 0.7 nm)$^{29}$, the number of the MoS$_2$ layers was determined to be 9 ~ 11. Figure 1d shows representative Raman spectra for the MoS$_2$ film. We observed E and A modes near 384 and 407 cm$^{-1}$, respectively. These data indicates that multi-layer MoS$_2$ was well deposited onto the waveguide surface$^{29}$.

To obtain a clear effect for the absorption of MoS$_2$ 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
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 waveguide. \(^2\)

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 MoS\(_2\) 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 MoS\(_2\).

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 below:\(^2\)

For TM waves

\[
1 + \frac{2\pi\sigma(\omega)\sqrt{c^2 - \omega^2}}{\omega c^2} = 0
\]

For TE waves

\[
1 - \frac{2\pi\sigma(\omega)}{\omega \sqrt{c^2 - \omega^2}} = 0
\]

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 party 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 MoS\(_2\) 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 MoS\(_2\) 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 MoS\(_2\). For the multilayer MoS\(_2\) film, the value of the indirect gap was over 1.20 eV corresponding to the little absorption in the near-infrared range. So there is hard to observe the optical absorption at the wavelength of 1064 nm.

By changing the thickness of the MoS\(_2\) film from \(-1.9\) nm to \(-39\) nm, we compared the absorption variation of the MoS\(_2\) 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 MoS\(_2\) film depended on the overlapping of the evanescent field and the MoS\(_2\) film. The absorption ratio of the MoS\(_2\) is supposed to be proportional to the intensity of the light in MoS\(_2\) described by the equation below:

\[
I_{abs} = C \times I_{MoS_2}
\]

where \(C\) is a parameter decided by the thickness of MoS\(_2\) film. \(I_{abs}\) is the power absorbed by MoS\(_2\) film and \(I_{MoS_2}\) is the power of the evanescent field overlapped with MoS\(_2\) film. According to the reconstructed refractive index distribution of the waveguide, we calculated the evanescent field of waveguide with different thickness of MoS\(_2\).

Figure 3b shows the refractive index distribution of the waveguide structure with a typical “enhanced well + optical barrier” shape, 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 \(\mu\)m. 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 MoS\(_2\) film. The variation of the evanesence field intensity in the MoS\(_2\) 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 MoS\(_2\) film. Through the interaction of an electromagnetic field with
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 ≈ 1.33), alcohol (n ≈ 1.35), or immersion oil (n ≈ 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 ~ 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 × 10 × 2 mm³ and optically polished. The carbon (C⁺) ions at energy of 6 MeV were implanted onto a 10 × 2 mm² surface at the fluence of 1 × 10¹⁵ 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 × 10 × 2 mm³. The biggest facets were optically polished. Two microfluidic channels with size of 5 × 2 × 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 split 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)¹⁰. 
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Measurement of waveguide propagation loss. The propagation losses ($\alpha_{\text{wa}}$) of the waveguide structure were measured by the back-reflection method. 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 MoS$_2$-waveguide absorption was shown in Fig. 1a. Through a microscope objective, the detecting light was coupled into the planar waveguide by the end-coupling method with a coupling efficiency of ~10%. And the output light from the waveguide structure was collected by a long-working distance microscope objective. Through the comparison of the input and output light power ($I_{\text{in}}$ and $I_{\text{out}}$), the loss induced by MoS$_2$ absorption ($\alpha_{\text{MoS}_2}$) was calculated by the equation below:

$$\alpha_{\text{MoS}_2} = 4.34 \ln \frac{I_{\text{out}}}{I_{\text{in}}} - \alpha_{\text{wa}}$$

Deposition and characterization of MoS$_2$ film. The MoS$_2$ film was fabricated by the pulsed laser deposition (PLD) with polycrystalline MoS$_2$ as the starting material. A KrF excimer laser (Comppex 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 MoS$_2$ film, both of the 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 MoS$_2$ film, both of the target and substrate were rotated and heated to 300°C during the deposition process. The topography of the MoS$_2$ 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.

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**Acknowledgments**
This work is carried out with the financial support by the National Natural Science Foundation of China (No. U1332121) and the 111 Project (No. B13029) of China.

**Author contributions**
Y.T., R.H., C.C., D.W., Y.C. and F.C. performed all the experiments and simulations. Y.T. and F.C. conceived the idea and designed the work. All the authors discussed the results and participated in the manuscript preparation.

**Additional information**
Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Tan, Y. et al. Polarization-dependent optical absorption of MoS2 for refractive index sensing. *Sci. Rep.* **4**, 7523; DOI:10.1038/srep07523 (2014).