

Research article

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Two-dimensional Bi_2S_3 -based all-optical photonic devices with strong nonlinearity due to spatial self-phase modulation

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Abstract: Bismuth sulfide (Bi_2S_3) is a binary chalcogenide semiconductor compound that has received much attention in optoelectronic devices because of its stratified structure. In this work we showed that the two-dimensional (2D) Bi_2S_3 shows strong nonlinearity using spatial self-phase modulation and that the all-optical photonic devices, e.g. the all-optical switches and all-optical diodes, have been demonstrated experimentally by observing the nonlinear behavior of the diffraction rings. In addition, an all-optical diode is designed in this work using combined structure with 2D $\text{Bi}_2\text{S}_3/\text{SnS}_2$ nanosheet by taking advantage of the reverse saturated absorption of 2D SnS_2 and saturated absorption of 2D Bi_2S_3 . Nonreciprocal light propagation has been achieved with different incident wavelength and a variety of incident intensities. Those characteristics make 2D Bi_2S_3 a potential candidate for the next generation nonreciprocal all-optical device.

Keywords: spatial self-phase modulation; all-optical diode; all-optical switch.

1 Introduction

Bismuth sulfide (Bi_2S_3) is a binary chalcogenide semiconductor compound belonging to the V–VI group with

a bandgap of 1.3 eV [1]. Thair et al. used aerosol-assisted chemical vapor deposition to synthesize Bi_2S_3 nanotube films with high photosensitivity and light response signals under illumination [2]. Bi_2S_3 nanosheet is considered as an excellent absorbing material [3] with an absorption coefficient of $\alpha \approx 10^5 \text{ cm}^{-1}$, and it has a wide range of applications in the field of nonlinear optics. Compared with other semiconductor materials, Bi_2S_3 has received much attention because of its stratified structure [4–6], which makes Bi_2S_3 a good candidate as photovoltaic devices, photoconductors, catalysis, and electrochemistry [7–11]. Conversely, SnS_2 is a IV–VI compound semiconductor belonging to the hexagonal crystal system (lattice constant $a = 0.365 \text{ nm}$, $b = 0.365 \text{ nm}$, and $c = 0.589 \text{ nm}$) with a bandgap of 2.6 eV [12]. With the strong optical absorption capability ($\alpha > 2 \times 10^4 \text{ cm}^{-1}$) [13], SnS_2 has been used as thin films for solar cell production. Additionally, the ultra-wideband and reverse saturated absorption (RSA) characteristic of SnS_2 have made it a proper material to design an all-optical diode device combined with other saturated absorption two-dimensional (2D) materials [12].

Spatial self-phase modulation (SSPM) is an effective way to study the nonlinear optical responses of a 2D material [14, 15] using diffraction rings [16]. Compared with the Z-scan technique by self-focusing or self-defocusing [17], the SSPM solution is more straightforward and easier to implement. By means of SSPM, the nonlinear coefficient of some 2D materials have been successfully measured, that is, graphene ($n_2 \approx 10^{-5} \text{ cm}^2 \text{ W}^{-1}$) [18], MoS_2 ($n_2 \approx 10^{-7} \text{ cm}^2 \text{ W}^{-1}$), WS_2 ($n_2 \approx 10^{-7} \text{ cm}^2 \text{ W}^{-1}$) [19], and black phosphorus ($n_2 \approx 10^{-5} \text{ cm}^2 \text{ W}^{-1}$) [20]. In this work, we obtained the nonlinear refractive index of Bi_2S_3 at different wavelengths using SSPM: $n_2 = 3.34 \times 10^{-5} \text{ cm}^2 \text{ W}^{-1}$ with $\lambda = 457 \text{ nm}$, $n_2 = 1.26 \times 10^{-6} \text{ cm}^2 \text{ W}^{-1}$ with $\lambda = 532 \text{ nm}$, and $n_2 = 1.62 \times 10^{-7} \text{ cm}^2 \text{ W}^{-1}$ with $\lambda = 671 \text{ nm}$. By taking advantage of strong nonlinearity and the diffraction effect of 2D Bi_2S_3 , an all-optical switching device has been designed based on the monochromatic light, which does not have time delay. The proposed switch has shown a faster optical

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response compared with other all-optical switches based on the cross-phase modulation [21–26].

Furthermore, it is known that diodes play an important role in electronic devices and systems, because of its unilateral conductivity characteristic. When the applied reverse voltage exceeds the threshold, the diode will breakdown and conduct a huge amount of current [27, 28]. In this paper, we also design a novel all-optical diode with the combined structure of 2D Bi₂S₃ and SnS₂. It is shown that when the laser beam passes the combined structure from the positive direction (Bi₂S₃/SnS₂), the diffraction rings are excited with a normal pattern, which can be considered as an “ON” state. However, if the laser beam passes the combined structure from the reverse direction (SnS₂/Bi₂S₃), no diffraction rings will be excited, representing the “OFF” state [29, 30].

2 Characterization and analysis of sample

Figure 1 shows the typical characterizations of the as-prepared Bi₂S₃ nanosheets fabricated by a liquid phase exfoliation method. According to the TEM images shown in Figure 1A, Bi₂S₃ nanosheets are successfully exfoliated with a lateral size ranging from 80 to 210 nm. The HRTEM images show clear lattice fringes of 0.27 and 0.31 nm (Figure 1B), which can be assigned to the lattice spacing in the (221) and (211) planes of Bi₂S₃, respectively [31, 32]. Moreover, a selected area electron diffraction (SAED) pattern (insert in Figure 1B) confirms that the crystal features of the Bi₂S₃ nanosheets keep in good order in liquid phase exfoliation. Additionally, the morphology and thickness of the as-prepared Bi₂S₃ nanosheets were determined by atomic force microscopy (Figure 1C–E). Individual thin Bi₂S₃ nanosheets in Figure 1C can be clearly observed, and their thicknesses are measured to be 7.2, 8.4, 13.8, and 15.3 nm (Figure 1E, D, and F), which correspond to 6, 8, 12, and 14 layers, respectively. The estimated thickness of monolayer Bi₂S₃ is 1.11 nm [33]. Ultraviolet-visible (UV-Vis) absorption spectroscopy was employed to characterize the optical response (Figure 1F). It can be clearly observed that the Bi₂S₃ nanosheets have a broadband absorption ranging from 250 to 1000 nm, which shows their great potential to be applied in UV-Vis-near infrared devices. It is worth to be noted that the obtained Bi₂S₃ nanosheets can still be re-dispersed in NMP (left picture in the Figure 1F left insert) and can be stabilized without any noticeable aggregation for more than 2 weeks at the room temperature. This

is verified by Tyndall effect (right picture in the Figure 1F left insert). During the procedure, the measured bandgap (E_g) energy increases from 1.30 (bulk Bi₂S₃) [34] to 1.68 eV (as-prepared Bi₂S₃ nanosheets; right insert in Figure 1F), which is in accordance with the previous reported results [35, 36]. The Raman spectra of the bulk Bi₂S₃ and Bi₂S₃ nanosheets are shown in Figure 1G. Fixed resonance peaks of bulk Bi₂S₃ are observed at 101.3 (A_g), 168.1 (B_{1g}), 186.2 (A_g), 238.0 (A_g), and 261.7 cm⁻¹ (B_{1g}), which agree well with the Raman bands reported by Huang [34] and Trentelman [37]. In addition, it is noticed that Bi₂S₃ nanosheets are red-shifted slightly compared with those of bulk Bi₂S₃ because of the larger free oscillation when fewer layers of Bi₂S₃ are bonded by van der Waals forces. This red-shift phenomenon is similar to the mode change of other 2D materials, such as black phosphorus and its analogue, beta-lead oxide [38, 39].

3 Experiment method and results

3.1 Schematic and experimental diagram of SSPM

Figure 2 shows the setup of the SSPM experiments. A laser beam emitted by a laser device passes the neutral optical attenuator, is then focused by a lens, and finally gets through the as-prepared sample (2D Bi₂S₃ dispersions). The optical response of Bi₂S₃ nanosheets resulted in a series of diffraction rings behind the cuvette. The laser device radiates at a fixed power, and the power of the incident light is adjusted using the optical attenuator. The optical lens focused the laser beam to a point, which enhanced the power density and helps excite the nonlinear effect from the 2D Bi₂S₃. The cuvette is used to hold the samples. Figure 1A demonstrates the nonlinear response of the 2D Bi₂S₃ dispersions for $\lambda = 457$ nm; the formation of the diffraction rings takes about 2.2 s. At the beginning, only a green point is formed behind the cuvette, and then the diffraction rings appear and reach the largest aperture after 0.88 s. The internal rings only sustain for a short period and then collapse gradually to half of the ring size at 2.2 s. This procedure shows that the nonlinear optical response of 2D Bi₂S₃ is a dynamic process for the CW laser, and the diffraction ring will eventually remain stable. Figure 1B and C show a similar process as Figure 1A, but the time periods from the formation of the diffraction rings to the collapse are different for each wavelength, and this is due to the different responsivities of 2D Bi₂S₃ dispersions with the various wavelength CW laser.

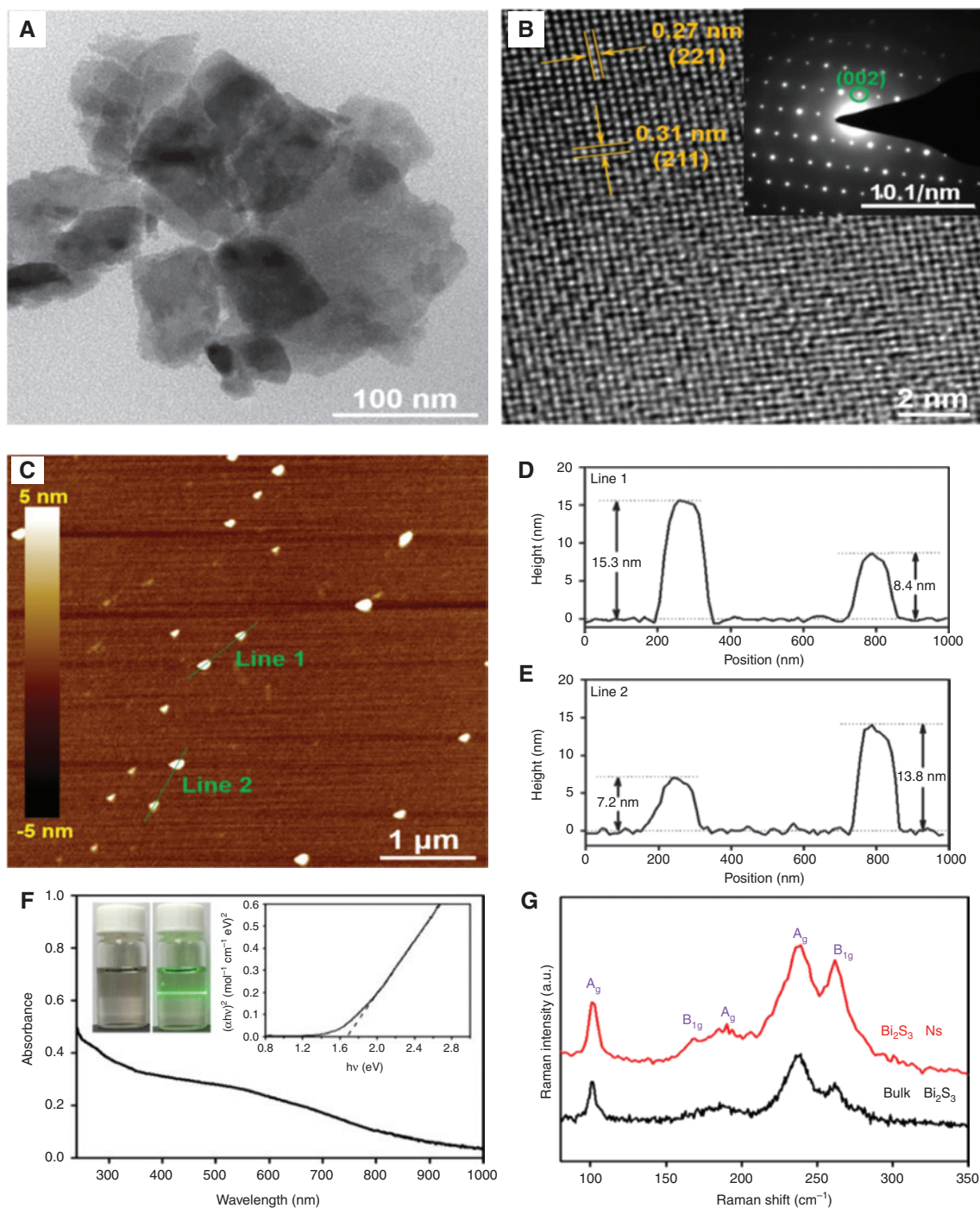


Figure 1: Structural characterization of the as-prepared Bi_2S_3 nanosheets.

(A) TEM image of the Bi_2S_3 nanosheets. (B) HRTEM image showing crystalline lattices. Inset: The selected area electron diffraction (SAED) pattern (up right). (C) AFM image of the Bi_2S_3 nanosheets. (D, E) Height profiles along the green lines in (C). (F) UV-Vis absorption spectrum of the Bi_2S_3 nanosheets in NMP. Left inset: Photos of the Bi_2S_3 nanosheet suspension (left) and the Tyndall effect of the Bi_2S_3 nanosheet suspension (right); right inset: Tauc plot for its calculation of the band gap (E_g) energy. (G) Raman spectra of bulk Bi_2S_3 and Bi_2S_3 nanosheets.

Based on the experiment of SSPM, we set a controlled trial, which is used to verify the relationship between thermal lens effect and optical nonlinearity. In Figure 3A, a chopper is placed behind the attenuator, and

it is able to produce a fixed-frequency laser beam, and its thermal lens effect is weaker than continue wavelength. Figure 3B shows the diffraction ring in modulator frequencies $f=0$ Hz, $f=20$ Hz, and $f=100$ Hz. According to these

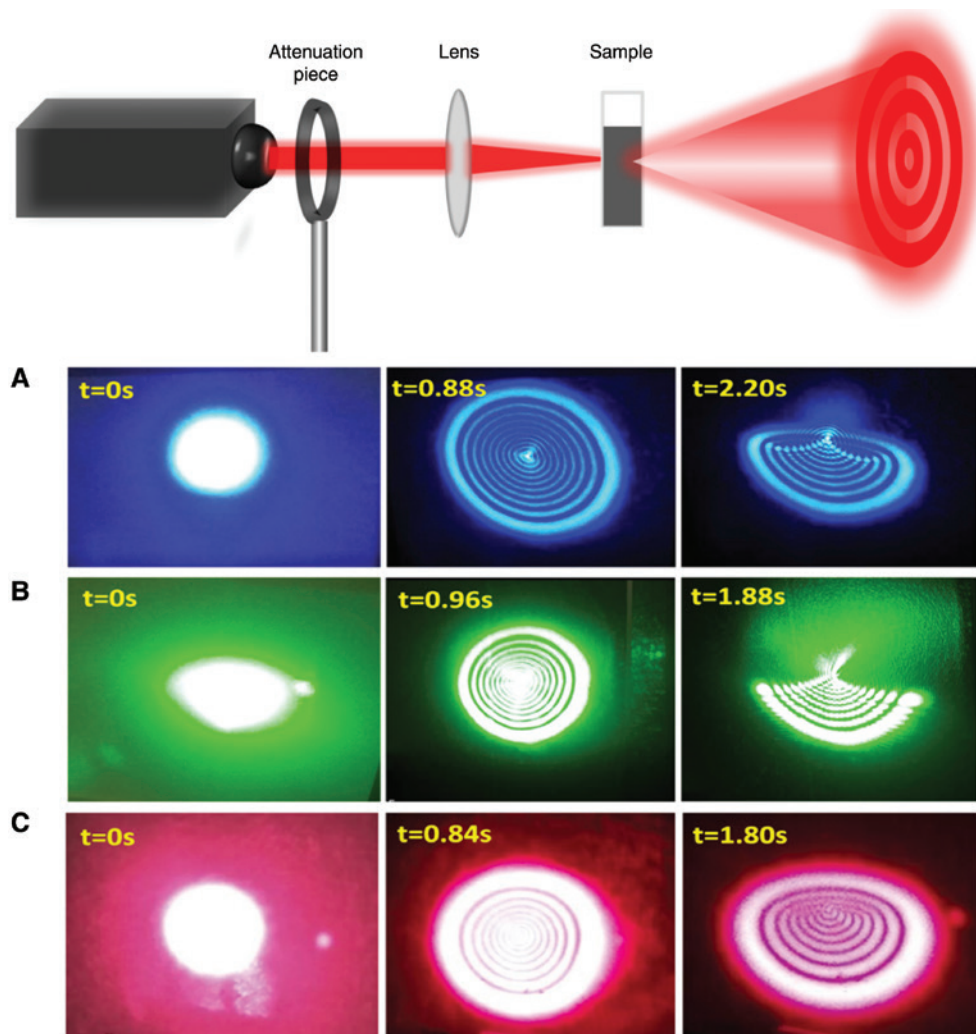


Figure 2: The experimental facility diagram of SSPM.

(A), (B), and (C) are the diffraction rings with $\lambda = 457, 532$, and 671 nm, respectively.

results, we can see that the number of diffraction rings in $f = 20$ Hz and $f = 100$ Hz is obviously less than the number of diffraction rings without chopper, which shows that the thermal lens effect plays an important role in optical nonlinearity. Therefore, we believe that both thermal lens effect and Kerr effect lead to the self-phase modulation and the diffraction ring.

3.2 Nonlinear refractive index of Bi₂S₃

From Kerr nonlinearity, we can obtain the equation based on optical nonlinear effect:

$$n = n_0 + n_2 I, \quad (1)$$

where $n_0 = 1.377$ stands for the linear refractive index of isopropanol, n_2 is the nonlinear refractive index of 2D Bi₂S₃

dispersions, and I is the incident intensity of laser beam. When the light passes through the 2D Bi₂S₃ dispersions, the nonlinear effect can be excited, and the phase shift can be expressed as follows:

$$\Delta\psi = \frac{2\pi n_0}{\lambda} \int_0^{L_{\text{eff}}} n_2 I(r, z) dz, \quad (2)$$

where L_{eff} is the effective optical thickness of 2D Bi₂S₃ dispersions. In addition, the radial coordinate $r \in (0, \infty)$ represents the distance from the focus point to the farfield, and $I(r, z)$ is the radial intensity distribution of the laser beam. According to the Gaussian beam theory, I (average intensity) is half of the central light intensity $I(0, z)$. In this experiment, the value of I can be adjusted. The number of rings (N) depends on $\Delta\psi(0) - \Delta\psi(\infty) = 2N\pi$. The expression of L_{eff} can be written as follows:

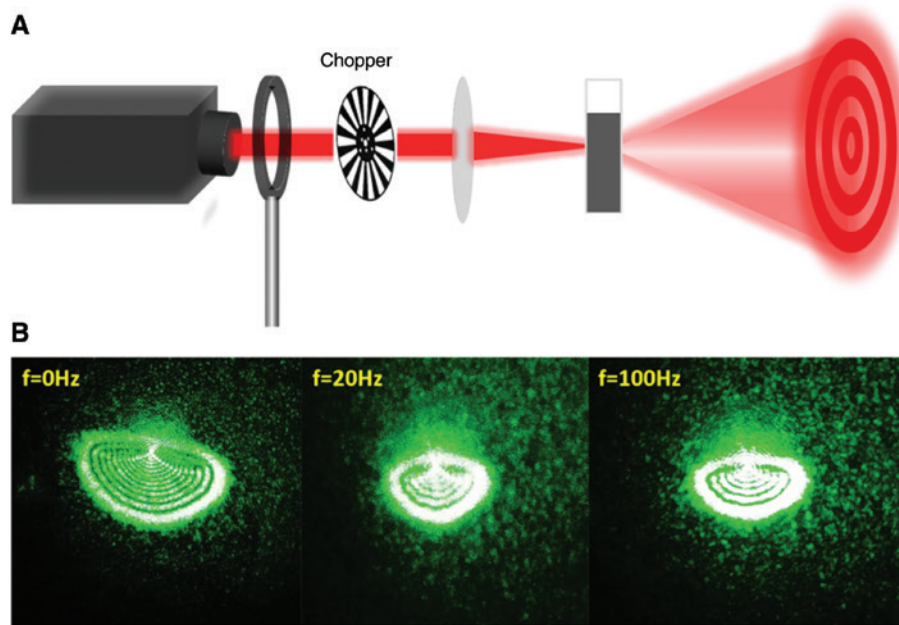


Figure 3: The contrast experiment with different incident intensity.

(A) The experimental facility diagram of SSPM and (B) the diffraction ring for the modulator frequencies of $f=0$ Hz, $f=20$ Hz, $f=100$ Hz.

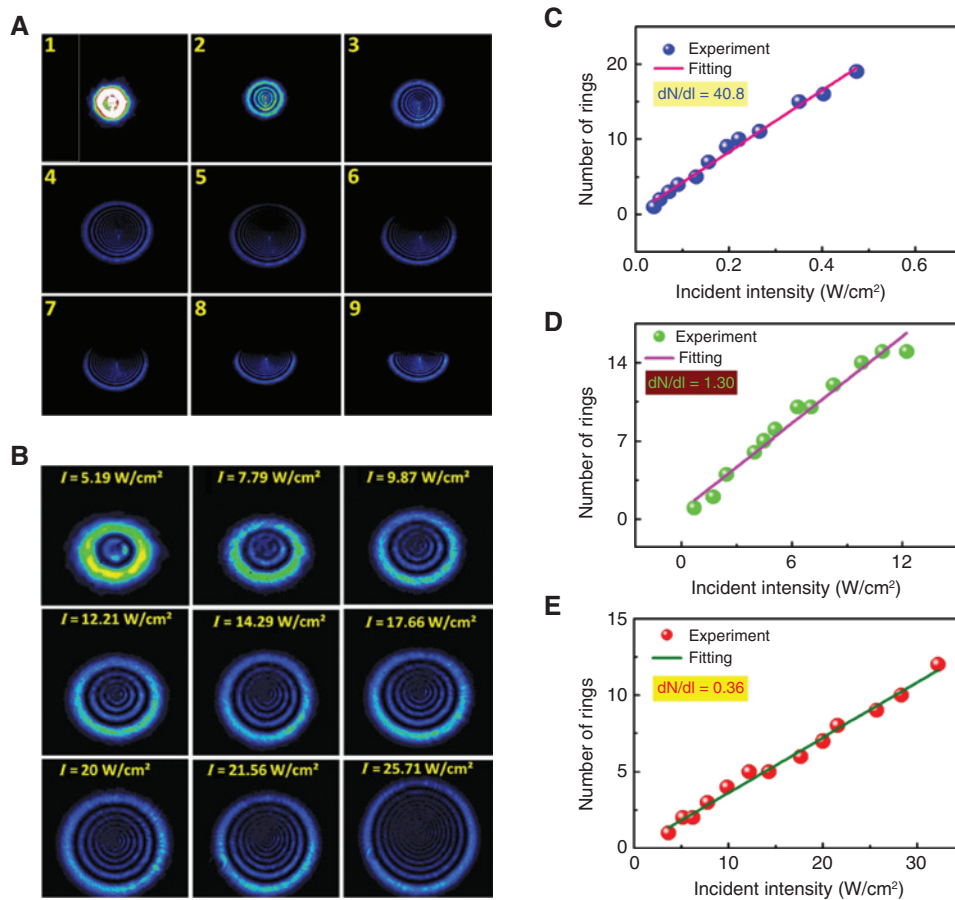


Figure 4: The experimental and data of SSPM.

(A) Whole process of diffraction ring, (B) the image of diffraction ring in variety incident intensity, (C), (D), and (E) are the number of the diffraction rings corresponding to the different incident intensity at $\lambda = 457$ nm, $\lambda = 532$ nm, and $\lambda = 671$ nm, respectively.

$$L_{\text{eff}} = \int_{L_1}^{L_2} \left(1 + \frac{z^2}{z_0^2} \right)^{-1} dz = z_0 \arctan \left| \frac{L_2}{L_1} \right|, \left(z_0 = \frac{\pi \omega_0^2}{\lambda} \right), \quad (3)$$

where L_1 and L_2 are distances from the local point to the front and rear surfaces of the quartz cuvette, respectively. Therefore, the cuvette's thickness is $L = L_1 - L_2$. ω_0 is the waist radius. In this work, $L = 1$ cm, and the focus of the lens $f = 10$ cm. As a result, the nonlinear index n_2 is given as follows [39]:

$$n_2 = \frac{\lambda}{2n_0 L_{\text{eff}}} \cdot \frac{N}{I}. \quad (4)$$

In this work, three different wavelengths are used to excite the nonlinear effect of Bi₂S₃, and Figure 4 shows the experimental results. Figure 4A illustrates the whole process (1–9) of the diffraction rings formation, from an initial point to the finally collapsed ring at $I = 25.71$ W/cm² with $\lambda = 671$ nm. Figure 4B shows the diffraction ring formed under various incident intensities when the diffraction rings are fully expanded. It is clear that the number of diffraction rings is closely related to the light intensity. Figure 4C shows the relationship between the number

of rings and incident intensity with $\lambda = 457$ nm. In this picture, the blue dots are the experimental data, and the red line is the fitted curve, where the slope $dN/dI = 40.8$. Similarly, Figure 4D and E show the dN/dI curves with $\lambda = 532$ nm and $\lambda = 671$ nm. According to these results, the nonlinear refractive indexes can be calculated, i.e. $n_2 = 3.34 \times 10^{-5}$ cm² W⁻¹ for $\lambda = 457$ nm laser, $n_2 = 1.26 \times 10^{-6}$ cm² W⁻¹ for $\lambda = 532$ nm laser, and $n_2 = 1.62 \times 10^{-7}$ cm² W⁻¹ for $\lambda = 671$ nm laser.

3.3 All-optical switch based on monochromatic light

All-optical switch based on the cross-phase modulation tends to have optical time delay. In this work, a novel all-optical switching device is proposed based on SSPM of 2D Bi₂S₃ with the monochromatic light, which eliminates the time delay. Figure 5A shows the experimental setup of the all-optical switch with $\lambda = 671$ nm laser. In the setup, a red laser beam passes through the attenuator and gets to the beam splitter, which divides the beam into two (pump and reference light). The pump laser beam then excites

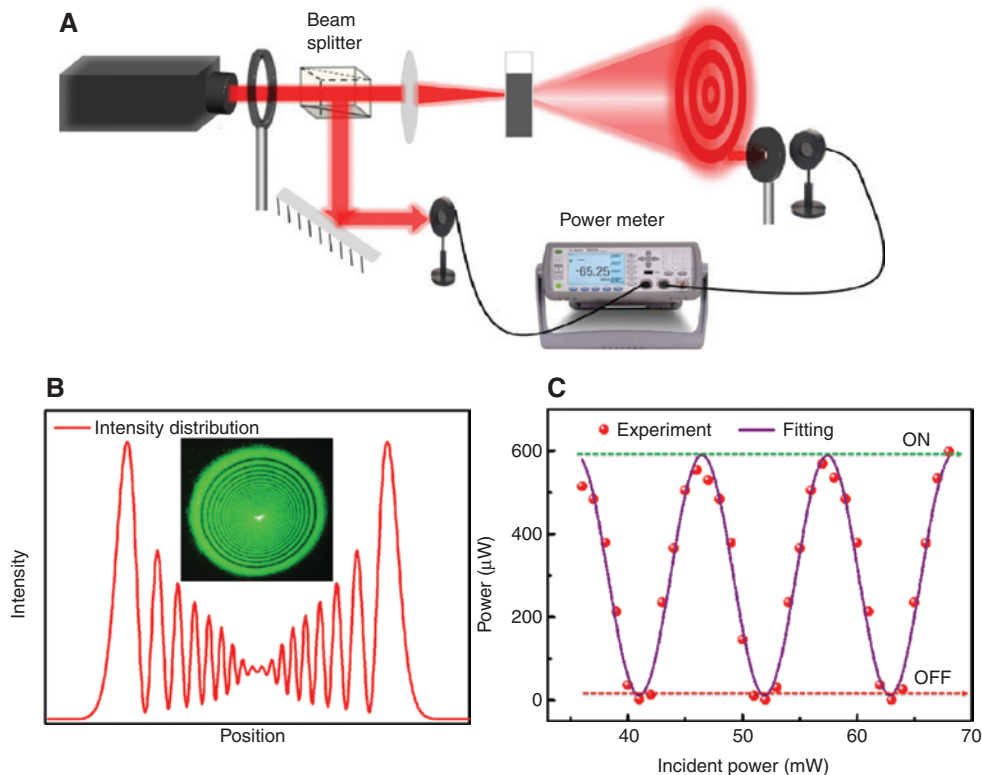


Figure 5: The theory and experiment of all-optical switch.

(A) All-optical switch schematic based on the monochromatic light, (B) theoretical intensity distribution of diffraction rings, and (C) experimental data of all-optical switch function.

the nonlinear effect of the 2D Bi_2S_3 sample, forming a series of diffraction rings. A diaphragm is placed at the outermost diffraction ring to monitor its power. Meanwhile, the power of the reference light is also recorded to compare with the pump light. Figure 5B illustrates the simulation result of the intensity distribution of diffraction rings, and it is found that the intensity reaches the peak value at the outermost ring and declines inward. To verify the simulated results, the intensity of each diffraction ring is measured using a power meter. The measured power distribution agrees with the simulated results. Figure 5C shows the plot of the experimental data of the all-optical switch function using discrete points. Different from the simulation, the incident intensity is adjusted using an attenuator to tune the position of the diffraction. During the procedure, the position of the aperture varies constantly between the dark and bright ring. When the aperture locates at the bright ring, the device is “ON”; in contrast, the dark ring stands for “OFF.” As a result, the all-optical switch function has been realized.

3.4 All-optical diode based on $\text{Bi}_2\text{S}_3/\text{SnS}_2$ nanosheets

Figure 6A shows the physical process of SSPM, where different lasers ($\lambda = 457, 532$, and 671 nm) are used to excite the nonlinear optical responses of 2D Bi_2S_3 . Because of the narrow bandgap of Bi_2S_3 (1.3 eV), all three laser beams are able to pump the photon from the valence band to the conduction band and generate the diffraction rings. However, SnS_2 has a bandgap of 2.6 eV, which requires more energy to pump photon. As depicted in Figure 6B, only the blue laser beam can excite the nonlinear effect and form a series of diffraction rings. Figure 6C illustrates the all-optical diode with a positive propagation of light. The laser beam first passes through the Bi_2S_3 , forming the diffraction ring, and then passes the SnS_2 , with a darker ring due to the reduced power. The response with a reverse propagation of light is shown in Figure 6D. In this case, the light first passes through the SnS_2 . However, because of the wide bandgap, no diffraction ring is formed. As an RSA

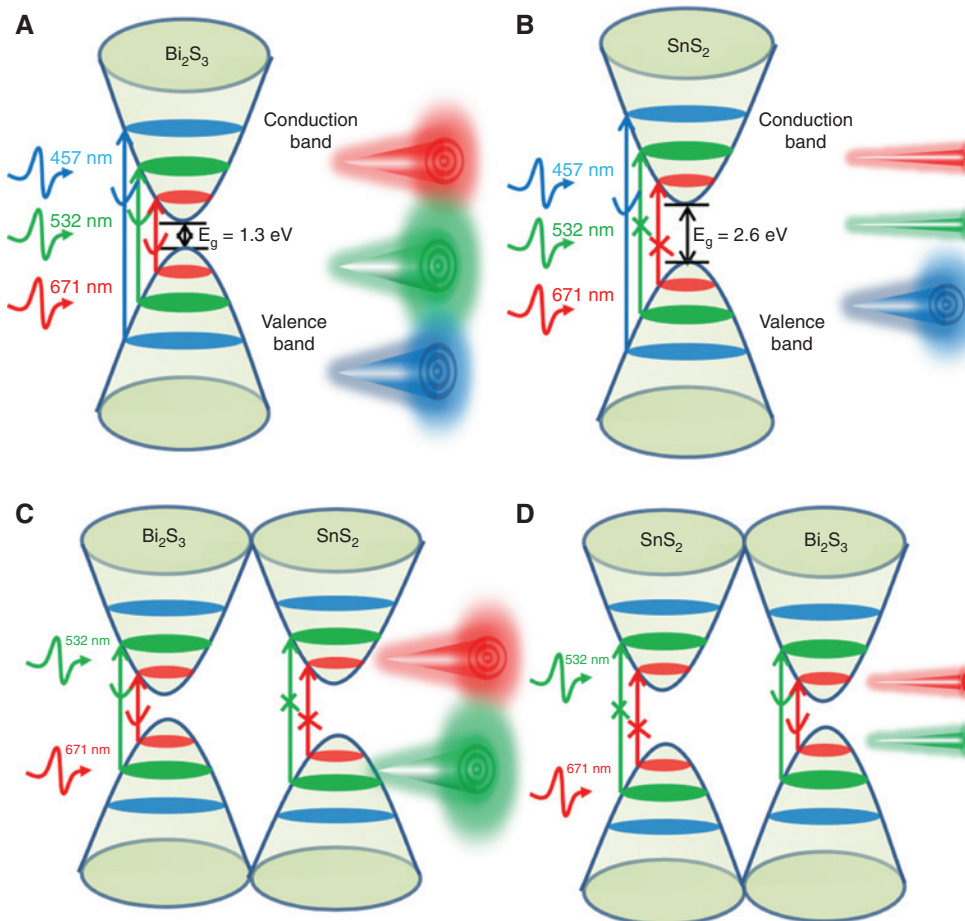


Figure 6: Microscopic principle of SSPM and all-optical diode.

(A) The schematic diagram of SSPM based on Bi_2S_3 ; (B) the schematic diagram of SSPM based on SnS_2 ; (C) positive propagation of light of all-optical diode; and (D) negative propagation of light of all-optical diode.

material, the SnS_2 greatly attenuates the power of the light passing through it, and thus, there is not enough energy to excite the nonlinear effect of subsequent 2D Bi_2S_3 .

Figure 7 shows the scheme of the all-optical diode. The measured result is consistent with the simulated results shown in Figure 6. In this experiment, the blue CW laser with $\lambda = 457 \text{ nm}$ is used together with the green and red CW laser for comparison. Different from the red and green CW lasers that have a lower energy and can only pass the device in the positive devices, the blue CW laser can excite the nonlinear effect of the composite construction from both positive and reverse directions. Therefore, we take advantage of the wide bandgap and RSA property of SnS_2 to design a novel all-optical diode bases on the combined 2D $\text{Bi}_2\text{S}_3/\text{SnS}_2$ dispersions, which is similar to the traditional electronic diode. By using the proposed structure, the uni-directional propagation of light can be easily implemented.

3.5 The relationship between incident intensity and all-optical diode

Figure 8A shows the nonlinear effect when three different CW lights pass through the 2D Bi_2S_3 dispersions; as a result, all of them excite the diffraction ring. It means that the 2D Bi_2S_3 has excellent optical response to these CW lasers. Figure 8A uses the composite structure of 2D $\text{Bi}_2\text{S}_3/\text{SnS}_2$. Compared with Figure 8A, it is found that when light passes the diode from the positive direction,

some diffraction rings are darker than the light that only passes the 2D Bi_2S_3 dispersions. In contrast, when light passes the diode from the reverse direction, there is no diffraction ring generated. Especially, the blue CW laser with $\lambda = 457 \text{ nm}$ is able to excite the nonlinear effect from both positive and reverse directions of the optical diode. Figure 8B shows the experimental results where the triangle stands for the measured number of diffraction rings, and the fitted line is plotted based on the measured discrete data. It can be seen that the number of diffraction rings generated from the positive direction of the optical diode is more than that from the reverse direction when $\lambda = 457 \text{ nm}$. This means that the 2D Bi_2S_3 has better optical response to incident light than SnS_2 . The experimental results agree with the theoretical values obtained in previous sections.

4 Conclusions

The 2D materials present excellent application in optics. In this work, we have studied the properties of 2D Bi_2S_3 and SnS_2 dispersions with aspects of bandgap, absorption, and nonlinear optical effect. We measured the nonlinear refractive index of 2D Bi_2S_3 by SSPM and investigated the relationship between incident intensity and nonlinear optical effect, which help to design the novel all-optical device. On the basis of the bright and dark diffraction rings generated from the different laser power, we

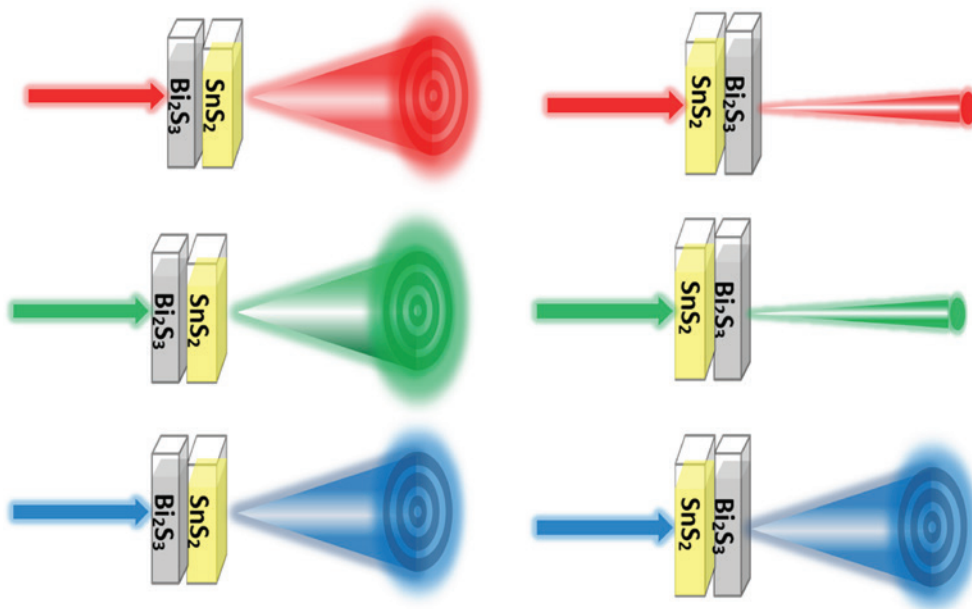


Figure 7: Experimental diagram of all-optical diode based on $\text{Bi}_2\text{S}_3/\text{SnS}_2$ with $\lambda = 457 \text{ nm}$, $\lambda = 532 \text{ nm}$, and $\lambda = 671 \text{ nm}$.

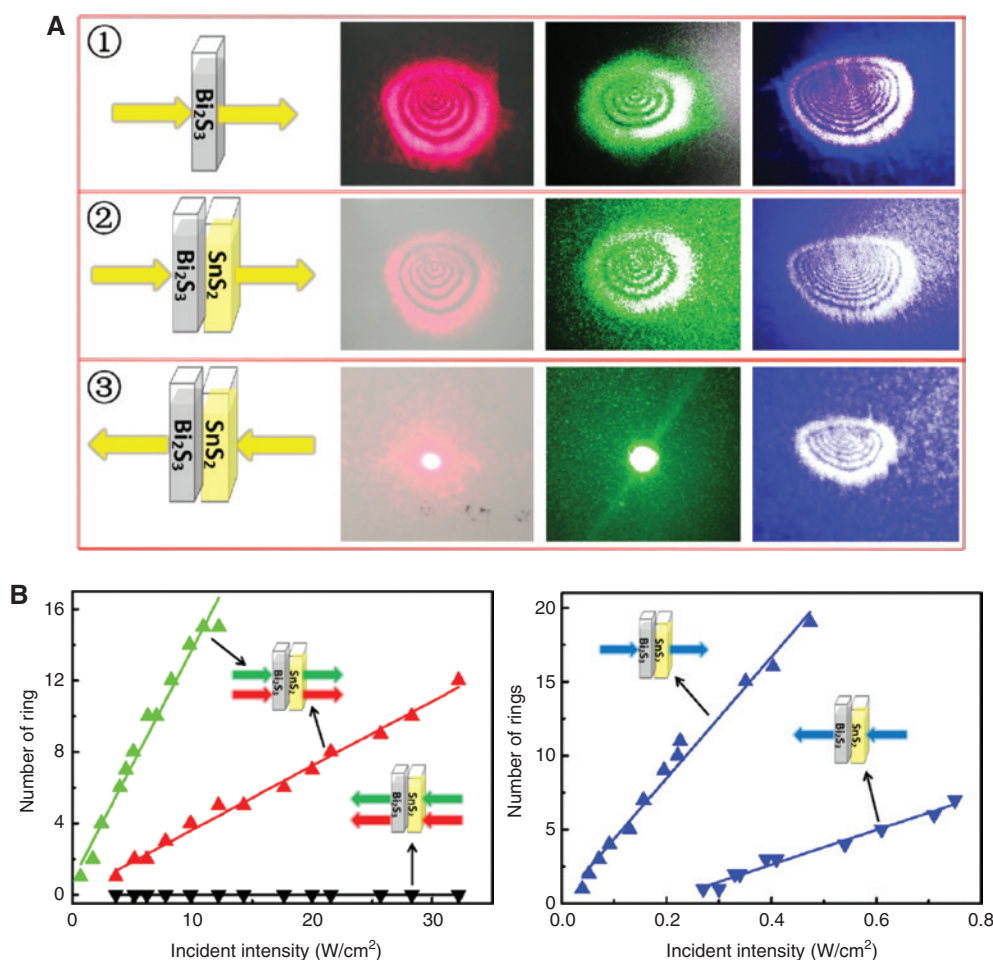


Figure 8: The experiment and data of all-optical diode.

(A) Experiments of all-optical diode with a different range of wavelength; (B) the experimental data of diode with $\lambda = 532 \text{ nm}$ and $\lambda = 671 \text{ nm}$, contrasting with $\lambda = 457 \text{ nm}$ based on the identical structure.

designed an all-optical switch by setting a threshold value of laser power of the diffraction ring. We have designed an all-optical diode with the combined structure ($\text{Bi}_2\text{S}_3/\text{SnS}_2$) by taking advantage of the RSA and wide bandgap properties of SnS_2 . We also investigated the nonlinear optical responses of SnS_2 with different laser wavelengths, further illustrating the importance of bandgap in SSPM. The results from this work may have potential applications in the future design of nonreciprocal all-optical device.

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