Nonlinear Coherent Light–Matter Interaction in 2D MoSe₂ Nanoflakes for All-Optical Switching and Logic Applications

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A strong nonlinear optical response of 2D MoSe₂ nanoflakes (NFs) through spatial self-phase modulation (SSPM) and cross-phase modulation (XPM) induced by nonlocal coherent light–matter interactions is reported. The coherent interaction of light and MoSe₂ NFs creates the SSPM of laser beams, forming concentric diffraction rings. The nonlinear refractive index \(n_2\) and third-order broadband nonlinear optical susceptibility \(\chi^{(3)}\) of MoSe₂ NFs are determined from the self-diffraction pattern at different exciting wavelengths of 405, 532, and 671 nm with varying laser intensity. The evolution and deformation of diffraction ring patterns are observed and analyzed by the “wind-chime” model and thermal effect. By taking advantage of the reverse saturated absorption of 2D SnS₂ NFs compared to MoSe₂, an all-optical diode has been designed with MoSe₂/SnS₂ hybrid structure to demonstrate the nonreciprocal light propagation. Few other optical devices based on MoSe₂ and semiconducting materials such as Bi₂Se₃, CuPc, and graphene have been investigated. The all-optical logic gates and all-optical information conversion have been demonstrated through the XPM technique using two laser beams. The proposed optical scheme based on MoSe₂ NFs has been demonstrated as a potential candidate for all-optical nonlinear photonic devices such as all-optical diodes and all-optical switches.

1. Introduction

Optical responses of 2D nanomaterials have drawn much attention due to their strong nonlinear characteristics and broadband Kerr nonlinearity for their potential applications in photonic devices. The strong light–matter interactions in 2D materials produce many interesting nonlinear optical phenomena, and quasiparticle excitations that can have far-reaching implications in science and technology. Therefore, 2D nanomaterials have attracted significant attention from fundamental physics to applied sciences as a scientific platform for studying nonlinear optical phenomena and optoelectronic devices. The nonlinear optical response has been investigated using the following three main methods that are four-wave mixing, Z-scan, and spatial self-phase modulation (SSPM) spectroscopy. The four-wave mixing and Z-scan spectroscopy require a complicated experimental setup, while similar results can be obtained in the SSPM with a simple, straightforward technique. Therefore, SSPM spectroscopy has become an effective tool for studying the nonlinear optical properties of the materials like nonlinear refractive index \(n_2\), and third-order nonlinear susceptibility \(\chi^{(3)}\). In this experiment, strong coherent light–matter interaction creates spatial phase modulation of the incident laser light and produces diffraction ring patterns in the far field. Durbin et al., first observed the SSPM in liquid crystals, and recently, in 2011, Wu et al., investigated the third-order nonlinear susceptibility in exfoliated graphene by the SSPM method. After that, there has been a significant increase in interest in SSPM, and many groups have studied the nonlinear response of different types of materials.

The nonlinear interaction of light and materials leads to self diffraction rings/patterns in the far-field due to the SSPM. The formation, expansion, and collapse process of the diffraction rings with time has been described by the “wind-chime” model based on the nonlocal electric coherent theory. In this model, the samples are being polarized because of interaction between the samples (layered nanostructures) and incident light.
coherent light beam. Based on the energy relaxation process, the samples are reoriented from an arbitrary angle to the direction of the electric field of the incident light beam. Although the above model describes the SSPM phenomena quite well, there are still a few open questions, like how the relaxation process occurs with incident light energy, how the relaxation time depends upon the solvent viscosity, and the role of polar and non-polar solvents? Therefore a detailed study of SSPM with different materials and solvents is desired for in-depth understanding.

Recently, a significant amount of work has been done on various 2D materials, such as graphene, topological insulators, perovskite, transition metal dichalcogenides (TMDs), MXenes, black phosphorus, etc., and different hybrid structures are also studied for photonic device application based on the SSPM method. The transition metal dichalcogenides (TMDs) are attractive candidates due to their unique tunable bandstructure and superior optic-electronic properties. TMDs are composed of transition metal elements intercalated between chalcogen elements in layered structures. In these materials, the adjacent layers are held together by the weak van der Waals forces. One of the most prevalent members of TMD’s family is MoSe2 which can be easily synthesized using various methods, including hydrothermal, sonochemical, chemical vapor deposition, etc. The MoSe2 are being widely explored for multiple potential applications, such as water splitting, catalysts, batteries, photoelectrochemical, solar cells, sensors, etc. However, the applications of MoSe2 in photonics are still in their infancy.

So far, the SSPM method has been used to determine the third-order nonlinear susceptibility and the nonlinear refractive index of various semiconducting materials, but comparatively few optical devices are made for practical applications. Very few groups have devoted their attention to making novel optical logic gates using the SSPM technique for photonic devices. These all-optical logic gates can open the paths toward many other all-optical signal processing such as optical networking, optical switching, optical computing, optical transmission, etc. Recently, all-optical switching and information converters based on SSPM have been demonstrated. However, there are no reports/works on photonic devices based on MoSe2 for all-optical logic applications.

In this work, we have experimentally investigated the nonlinear optical (NLO) properties of 2D MoSe2 nanoflakes (NFs) using SSPM spectroscopy and designed a novel photonic diode. Furthermore, we have also presented a hybrid structure-based optical device for the realization of the “OR” function for all-optical logic gates. We believe that this study will enhance the understanding of the nonlinear optical process in 2D materials and can lead to the development of optical devices based on the self-diffraction of light.

2. Results and Discussion

2.1. Nonlinear Kerr Effect: Nonlinear Refractive Index of MoSe2 Nanoflakes

The preparation of MoSe2 NFs and its characterization are discussed in the Experimental Section and presented in Figure 1. The Kerr nonlinear effect plays an important role in the study of the nonlinear optical response of 2D semiconducting (MoSe2) materials. According to the nonlinear Kerr effect, the nonlinear refractive index can be expressed as \( n = n_0 + n_2 I \), where \( I \) is the incident light intensity, \( n_0 \) and \( n_2 \) are the linear and nonlinear refractive index coefficient of the material, respectively. The MoSe2 is expected to have a strong Kerr nonlinear response. Therefore, the phase has a nonlinear modulating behavior to the transverse intensity profile of the incident Gaussian laser beam, and this nonlinear phase shift (\( \Delta \psi \)) can be expressed by

\[
\Delta \psi(r) = \frac{2\pi n_2}{\lambda} \int_0^{L_{\text{eff}}} n_1 I(r, z) \, dz
\]

where \( \lambda \) is the wavelength of the laser, \( r \in [0, +\infty) \) is the laser radial position, \( L_{\text{eff}} \) is the effective transmission length of the laser passing through the cuvette. This “self” phase shift \( \Delta \psi \) gets modulated due to the nonlinear Kerr effect through the change in optical refractive index, \( n_2 \) as function intensity of the coherent Gaussian laser beam. Therefore, the propagating beam forms self-diffraction patterns in the far-field due to the spatial self-phase modulation (SSPM). The schematic representation of SSPM due to the light–matter interaction between the incident laser beam and the reoriented MoSe2 NFs is shown in Figure 2b. There are at least two different points \( r_1 \) and \( r_2 \) in the resultant outgoing Gaussian light, where the slopes of the distribution curve are same \( (d\Delta \psi / dr)_{r_1} = (d\Delta \psi / dr)_{r_2} \) and they have same phase. Therefore, the output light intensity profile with the same slope points maintains constant phase differences. The diffraction ring patterns are either bright or dark as given by the following condition.

\[
\Delta \psi(n_2) - \Delta \psi(n_2) = 2M\pi
\]

where \( M \) is the integer number. The odd and even values of the \( M \) correspond to the dark and bright diffraction ring, respectively. Also the path difference, \( L_{\text{eff}} \) of the laser beam inside the cuvette can be determined from the following equation

\[
L_{\text{eff}} = \int_0^{L_2} \left( 1 + \frac{z^2}{z_0^2} \right)^{1/2} \, dz = z_0 \tan^{-1}\left( \frac{z}{z_0} \right) + \frac{\pi \omega_0^2}{\lambda}
\]

where \( L_1 \) and \( L_2 \) are the distance from the focus (f) to the sides of the quartz cuvette. The central intensity profile of the transmitted Gaussian beam can be expressed as \( I(0, z) = 2I \), where \( I \) is the average intensity of the incident laser, \( z_0 \) is the diffraction length and \( \omega_0 \) is the 1/e² beam radius. From Equations (1) and (3), the nonlinear refractive index \( n_2 \) of MoSe2 NFs can be determined as

\[
n_2 = \frac{\lambda}{2n_0 L_{\text{eff}}} \frac{dN}{dI}
\]

Here, \( \frac{dN}{dI} \) is a crucial parameter for determination of the NLO refractive index of 2D materials. Hence, the third-order nonlinear susceptibility, \( \chi^{(3)} \), can be determined for MoSe2 NFs using the NLO properties as.
where \( c \) is the velocity of light in the free space. However, the available number of active 2D NFs of MoSe\(_2\) present in the solvent has put a significant role on total \( \chi^{(3)} \), so it is necessary to determine the third-order nonlinear susceptibility for a single-layer \( \chi^{(3)}_{\text{monolayer}} \). Hence, the \( \chi^{(3)} \) for the single-layer MoSe\(_2\) can be determined by:

\[
\chi^{(3)}_{\text{total}} = \frac{c n^2}{12\pi^2} 10^{-7} n_2 \text{ (esu)}
\]  

where \( n \) represents the effective number of layers of material. This \( \chi^{(3)} \) has a strong dependence on the electric field strength of the incident laser beam. The detailed calculation has been provided in the Supporting Information.

The Figure 2c shows the diffraction ring patterns projected on the screen as a function of intensity of the incident light (\( \lambda = 671 \text{ nm} \)). With the increasing intensity of the incident light, the horizontal diameter of the rings and also the ring numbers increase linearly. The same experiment has been repeated for the other two lasers of \( \lambda = 532 \) and \( 405 \) nm and the results are presented in Figure 2d. Figure 2d shows the variation of the diffraction ring numbers as a function of the intensity of the laser beams. From the linear fitting of the corresponding data, the estimated slopes \( \frac{dN}{dI} \) are 0.9765, 2.3155, and 9.4999 for \( \lambda = 671, 532, \) and \( 405 \) nm, respectively. The results reveal that \( \frac{dN}{dI} \) increases with decreasing wavelength of the laser lights. Here, the larger photon energy gives rise to higher SSPM effects consistent with other previously reported results. NLO responses of 2D materials are dependent not only on the photonic energy but also on a few other parameters, like available active materials and the effective length travel by the laser inside the medium. To study this effect, the concentration of MoSe\(_2\) and the cuvette thickness have been varied.
Figure 2e shows the variation of the diffraction ring numbers as a function of laser light intensity with $\lambda = 671$ nm for three different cuvette thicknesses. The number of diffraction rings has a dependence on the thickness of the cuvette, and their slopes are found to be 0.9765, 0.8373, and 0.3807 for cuvette length $L = 10$, 5, and 1 mm, respectively. The corresponding diffraction ring patterns at highest intensity are presented in Figure 2e. Hence, the available light– matter interaction due to the presence of active materials inside the medium is also studied, as a function of laser light intensity with $\lambda = 405, 532$, and 671 nm.

Figure 2f shows the variation of the diffraction ring numbers with incident laser ($\lambda = 671$ nm) intensity with cuvette lengths of 1, 5, and 10 mm. The diffraction ring number versus intensity of laser ($\lambda = 671$ nm) with various concentration of MoSe$_2$ (0.25, 0.0625, and 0.03125 mg mL$^{-1}$). The diffraction images for the highest intensity are shown in Figure 2f for $C = 0.25$, 0.0625, and 0.03125 mg mL$^{-1}$, respectively. From the above experiments, the $n_2$ and $\chi^3$ values are calculated and presented in the Table 1. As evident from the results, the increment of $n_2$ and $\chi^3$ occurs due to an increase in the energy of the incident laser beam and the active material concentration. These results reveal that both $n_2$ and $\chi^3$ increase with the increasing energy of the incident laser beam. Whereas with reducing the effective travel length of the laser beam inside the medium by changing the thickness of the cuvette, $n_2$ and $\chi^3$ values are also increased. Similarly, with increasing the concentration of the active material, the $n_2$ and $\chi^3$ values are also increased.

Here, we have observed that the number of diffraction rings increases with increasing cuvette thickness and the concentration of MoSe$_2$ NFs. The above results can be understood from the interaction of light with the suspended NFs. The
variation of $\chi^{(3)}$ and $n_2$ are similar in nature, as suggested from Equation (5), whereas $n_2$ has strong dependence on $\lambda$ of incident laser, effective transmission length of the laser propagating through the medium and generates from the light–matter interaction. The electrons of the NFs coherently oscillate due to the strong light–matter interaction. With the increasing cuvette thickness or NFs density in the solution, effective interaction of the laser beam with materials increases. These results are observed due to the larger spatial phase shift of the laser beam leading to create more diffraction rings.

The obtained $n_2$ and $\chi^{(3)}$ for MoSe2 NFs are found to be comparatively larger than other family members of transition metal dichalcogenides (TMDs) (see Table 1 and Section S2 in the Supporting Information). The larger NLO responses compared to other TMDs can be attributed to the morphological changes and large surface area of MoSe2.[45]

### 2.2. SSPM: Mechanism of Light–Matter Interaction

In the above-mentioned nonlinear Kerr effect leading to SSPM, the $n_2$ and $\chi^{(3)}$ are determined for the suspended MoSe2 NFs. The self-phase modulated diffraction ring numbers increase with time to a maximum value. The time required to achieve that maximum diameter at a fixed intensity is described by the “wind-chime” model proposed by Wu et al.[15] According to this model, the time required to form the maximum diameter full circular diffraction pattern is equal to the time required to reorient these NFs along the electric field of the incident polarized light. The time evolution of the diffraction ring numbers is presented in Figure 3e, and the dynamics of formation diffusion rings follow the exponential model as,

$$N = A(1 - e^{-\tau/T})$$  \hspace{1cm} (7)

where $N$ is the number of rings, $\tau$ is the rise time for the ring formation, and $A$ is a constant. As shown in Figure 3e, the $\tau$ is estimated to be 0.209, 0.317, and 0.0039 s for 671, 532, and 405 nm, respectively. The minimum time ($T$) required for reaching the highest number of rings is estimated to be 0.41, 0.62, and 0.74 s, respectively. According to the wind-chime model, the time required for the pattern formation is as follows[13,17]

$$T = \frac{e, \eta \epsilon \sqrt{\frac{Rc}{1.72(\epsilon_0 - 1)\eta}}}{\frac{6}{\lambda h}}$$  \hspace{1cm} (8)

where $\epsilon$ is the relative dielectric constant of MoSe2, $\eta$ is the coefficient of viscosity of the solvent, $R$ is the domain radius ($=100 \text{nm}$), $h$ is the flake thickness ($=5 \text{nm}$), and $I$ is the laser intensity ($=12 \text{W cm}^{-2}$). As we know that the formation time of diffraction ring (Equation (8)) strongly depends on the size, thickness, and dielectric constant of the materials. Also, $T$ depends upon the viscosity ($\eta$) of the dispersion medium, and they are proportional to each other. Hence, keeping all the parameters same, if we use solvents with different viscosity, the formation time of those diffraction rings are also different. Low viscous medium requires a shorter time to reorient the 2D NFs toward incident electric field rather than high viscous medium. To verify the wind-chime model, two different viscous medium like NMP ($\eta = 1.65 \times 10^{-3} \text{ Pa s}$) and acetone ($\eta = 3.2 \times 10^{-4} \text{ Pa s}$) have been chosen. As expected, the theoretically estimated $T$ is found to be 0.38 and 0.26 s for NMP and acetone solvent, respectively. Also, the $T$ is estimated from the experimental data (Figure 3f) to be 0.41 and 0.22 s for NMP and acetone solvent, respectively. The experimental results are in good agreement with the previously reported values for other materials, as presented in Table 2.

To investigate the effect of polarity of the solvent, we have used one polar (NMP) and one non-polar (toluene) solvents

| $\lambda$ [nm] | $L$ [mm] | $C$ [mg mL$^{-1}$] | $\frac{dN}{dt}$ [cm$^2$ W$^{-1}$] | $n_2$ [cm$^2$ W$^{-1}$] | $\chi^{(3)}$ [esu] | $\chi^{(3)}$ [esu] |
|----------------|-----------|----------------|---------------------|---------------------|----------------|----------------|
| 671            | 10        | 0.0625         | 0.97562             | $6.6 \times 10^{-6}$ | 0.00428        | 1.35 $\times 10^{-8}$ |
| 532            | 10        | 0.0625         | 2.3155              | $1.3 \times 10^{-5}$ | 0.00706        | 2.23 $\times 10^{-4}$ |
| 405            | 10        | 0.0625         | 9.49993             | $6.1 \times 10^{-5}$ | 0.01357        | 4.86 $\times 10^{-4}$ |
| 671            | 5         | 0.0625         | 0.83735             | $1.1 \times 10^{-5}$ | 0.00735        | 3.25 $\times 10^{-4}$ |
| 671            | 1         | 0.0625         | 0.38072             | $2.6 \times 10^{-5}$ | 0.01672        | 5.29 $\times 10^{-4}$ |
| 671            | 10        | 0.1375         | 1.41262             | $9.6 \times 10^{-6}$ | 0.00629        | 1.96 $\times 10^{-8}$ |
| 671            | 10        | 0.03125        | 0.73344             | $4.9 \times 10^{-6}$ | 0.00322        | 1.01 $\times 10^{-4}$ |
keeping other parameters constant. The results are presented in Figure 3g. In both cases, similar diffraction patterns are observed, which confirms that these NLO effects are truly the properties of 2D semiconducting materials, and the nature of polarity of the solvent doesn’t play any role.

In addition to the Kerr nonlinearity, the change in the temperature of the medium under an intense laser beam can also modify the refractive index of the medium and produce similar self-phase modulation as described above. The above phenomenon is known as the “thermal lens effect.” In our experiments, the chopper can modulate the intensity of the laser at a frequency of 20–400 Hz.

SSPM is an NLO phenomenon and depends on the reorientation or polarization of the materials with an incident laser beam. In contrast, the thermal lens effect has a linear optical response. To confirm the origin of the diffraction rings, a mechanical chopper was introduced into the path of the incident laser beam. In our experiments, the chopper can modulate the intensity of the laser at a frequency of 20–400 Hz.
rings after using the chopper is less than those without a chopper. These observations confirm that the NLO response is the inherent feature and dominates the thermal lens effect.

### 2.3. Dynamics of Collapse Phenomena of Diffraction Patterns

After a close look, it has been observed that the diffraction rings are getting distorted with time. In the SSPM experiment, the diffraction ring gradually develops once the focused laser passes through MoSe$_2$ NFs. After the diffraction ring reaches its maxima, the upper half of the vertical radius begins to collapse toward the center. More distortion occurs along the vertical direction compared to the horizontal direction, as shown in Figure 4a. To be more precise, the lower half of the diffraction rings remained stable, whereas the upper half collapses. After a few seconds, it reaches the equilibrium situation as shown in Figure 4a. This collapse (upper half) process is due to the non-axis-symmetrical thermal convection leading to the distortion of diffraction pattern described by Wang et al.[42]. In this process, the dispersive medium absorbs some part of the propagating laser light due to its finite optical absorption coefficient.[14,49] As a result, the temperature gradient increases along the vertical direction around the laser spot, enhancing the thermal convection process.[50] The above convection process of the medium reduces the concentration of the 2D materials in the upper part of the medium compared to the lower part. Therefore, the upper part of the laser beam is less diffracted by the dispersed 2D materials leading to distorted diffusion patterns which collapse toward the center. The above phenomenon is quantified by the half-cone angle of the diffraction pattern of the Gaussian laser beam, which can be expressed as

$$\theta = \frac{\theta_{\text{ic}} - \theta_{\text{c}}}{2 \Delta \theta}$$

$$\frac{R_D}{D} = \frac{R_H}{D}$$

where $R_H$ is the maximum diffraction radius, $\theta_{\text{ic}}$ is the maximum half diffraction angle. After the distortion, the two parameters $R_D$ and $\theta_D$ must be changed to new values of $R_{\text{ic}}^*$ and $\theta_{\text{ic}}^*$, respectively, and $\theta_D$ can also be described as a difference of nonlinear refractive index as

$$\theta_D = \theta_{\text{ic}} - \theta_{\text{c}} = (n_2 - n_1^*) IC = \Delta n IC$$

Therefore, the final relation between the relative change in nonlinear refractive index can be presented in terms of the ratio between the distorted and maximum half-angle as

$$\frac{\Delta n_2}{n_2} = \frac{\theta_D}{\theta_{\text{ic}}}$$

Based on Equation (12), the distortion process of the diffraction rings is qualitatively analyzed by $\Delta n_2/n_2$ with the dynamic change of the distortion and full radius of the diffraction rings ($R_D/R_{\text{ic}}$). Typically, the $\Delta n_2/n_2$ mainly depends on the laser intensity, temperature, and time.[1] Among the above three parameters (intensity, temperature, and time), the intensity of the laser beam has the most prominent dependence on the change of the nonlinear refractive index ($n_2$).[51,54]

Figure 4a (b,d) shows the image of the diffraction ring patterns after attaining the maximum size and at the steady-state condition after the collapse process for the laser beam with $\lambda = 671$ nm. Figure 4b–d shows the evolution of the diffraction ring pattern over time for all three laser beams with $\lambda = 671, 532$, and 405 nm, respectively, at their highest intense laser power. For all three lasers, the horizontal diameters increased to the maximum diameter during the expansion and remained constant for the rest of the time. At the same time, the vertical diameters reach the maximum size and then slowly collapse with time to steady-state values. Interestingly, the collapse time increases (0.54, 0.89, and 1.06 s) with the increasing photon energy of the laser beam ($\lambda = 671, 532$, and 405 nm). The experimentally measured maximum vertical radius ($R_{\text{ic}}$) before the collapse and the radius after the collapse process ($R_0$) are presented in Figure 4e.f. Here, during the collapse process, the deformation of the diffraction rings are observed due to non-axis-symmetrical thermal convection as described above.

### Table 2. Diffraction ring formation time from “wind-chime” model.

| Materials          | Solvent | Wavelength $\lambda$ [nm] | Intensity $I$ [W cm$^{-2}$] | Formation time $T$ [s] | Refs. |
|--------------------|---------|--------------------------|-----------------------------|------------------------|-------|
| MoS$_2$            | NMP     | 532                      | 250                         | 0.2                    | [15]  |
| MoTe$_2$           | NMP     | 750                      | 252                         | 0.62                   | [46]  |
| Black phosphorus   | NMP     | 700                      | 18.9                        | 0.7                    | [17]  |
| Graphite           | NMP     | —                        | 100                         | 0.43                   | [8]   |
| MoSe$_2$           | NMP     | 671                      | 12                          | 0.41                   | This work |
| MoSe$_2$           | Acetone | 671                      | 12                          | 0.22                   | This work |

Figure 4a shows the schematic presentation of the time-dependent collapse process by changing the diffraction angle. The intensity-dependent collapse behavior of the diffraction rings can be quantified by the change of diffraction angle formed between the sample and the screen.[23] These diffraction rings are formed through a series of coaxial cones, and the distortion angles are presented as

$$\Delta \theta_D = \theta_D - \theta_{\text{ic}}$$
Figure 4 shows the dependence of relative change in the nonlinear refractive index with the incident laser beam intensity using Equation (12). The $\Delta n_2/n_2$ increases with increasing laser light intensity, but the relative change tends to be saturated with the increasing laser light intensity. The nonlinear effect of blue light is the strongest. The relative nonlinear refractive index $\Delta n_2/n_2$ of the MoSe$_2$ NFs is found to be 40% (2 W cm$^{-2}$), 75% (12.5 W cm$^{-2}$) and 60% (12 W cm$^{-2}$) for the incident light with $\lambda = 405, 532$, and 671 nm, respectively.

### 2.4. Nonreciprocal Light Propagation in MoSe$_2$ Based Photonic Diode

Here we demonstrate a novel nonlinear photonic diode device using MoSe$_2$/SnS$_2$ hybrid structure based on the SSPM. The SnS$_2$ is another nonlinear material that shows strong NLO response and SSPM. The SnS$_2$ has a bandgap (2.6 eV) larger than MoSe$_2$ (1.6 eV) and the hybrid structure can be used as a photonic diode for nonreciprocal light propagation.$^{[39,40]}$ The laser lights with $\lambda = 532$ and 671 nm are used to characterize the photonic diode based on MoSe$_2$/SnS$_2$ hybrid structure. The photonic diode produces the diffraction pattern when the laser beams propagate in the forward direction (i.e., MoSe$_2$ $\rightarrow$ SnS$_2$) as shown in Figure 5a ($\theta$, $\Phi$, $\delta$). Whereas in the reverse direction (i.e., MoS$_2$ $\leftarrow$ SnS$_2$), no such diffraction rings are observed as shown in Figure 5a ($\theta$, $\Phi$, $\delta$). In the reverse direction large absorption through SnS$_2$ reduces the intensity of the laser in MoS$_2$. Therefore, the effect of SSPM is negligible and there are no diffraction patterns. Therefore the above properties of proposed hybrid photonic diode can be used for all-optical switch applications where the nonreciprocal propagation of light can be achieved.

Laser light intensity-dependent diffraction ring numbers with unidirectional property of MoSe$_2$/SnS$_2$ photonic diode for laser beams with $\lambda = 671$ and 532 nm, are presented in Figure 5b,c.
Here the values of $dN/dI$ are found to be 1.479 and 0.9186 for $\lambda = 532$ and 671 nm, respectively. The values are very much comparable with single MoSe$_2$ results. The photonic diode has a higher NLO response at $\lambda = 532$ nm than $\lambda = 671$ nm, and it can perform better as an optical diode at a higher wavelength.

To further check the unidirectional performance of the nonlinear photonic diode (using $\lambda = 405$ nm), SSPM experiments have been performed in both forward and reverse operation and results are presented in Figure 5d. Interestingly, the diffraction rings appear in both directions, but the number of diffraction
rings is different. Therefore, the MoSe\textsubscript{2}/SnS\textsubscript{2} photonic diode is not appropriate for lower \( \lambda \) like 405 nm, and to investigate it, we have performed the SSPM for only SnS\textsubscript{2} using 405 nm laser and results are shown in Figure 5e. As expected, the SSPM is observed in SnS\textsubscript{2} (bandgap \( \approx 2.6 \) eV) when the laser with higher excitation energy (2.71 eV) is applied\textsuperscript{[27]} To understand the basic mechanism for photonic diode application through the light–matter interaction, schematically, we present the energy band for both MoSe\textsubscript{2} and SnS\textsubscript{2} in Figure 5f,g for forward and reverse, respectively.

In this experiment, three different lasers having higher energy than MoSe\textsubscript{2} (bandgap \( \approx 1.6 \) eV) are used, and a photon of energy \( E = \hbar \omega \) can excite the electrons from the valance band to the conduction band. The excited electrons go to the ground state by releasing the photon. The emitted photons interact with the incident light and produce the diffraction rings through the optical Kerr effect\textsuperscript{[19,27]} In this process, the excited electrons will move antiparallel with the applied optical electric field (coming from the laser beam) and polarize the suspended MoSe\textsubscript{2} NFs. Next, the reorientation process reduces the angle between the polarization direction and the external electric field to achieve the minimum interaction energy configuration. That increases the NLO response of 2D MoSe\textsubscript{2} NFs, leading to the nonlinear Kerr effect\textsuperscript{[32,33]}

However, 532 and 671 nm lasers are unable to excite the electrons in SnS\textsubscript{2} from valance band to conduction band and mostly get absorbed due to the intraband transitions. Therefore, no such diffraction rings are observed\textsuperscript{[2,19,24]} The laser beam with \( \lambda = 405 \) nm produces diffraction rings in both the pure SnS\textsubscript{2} system as well as the MoSe\textsubscript{2}/SnS\textsubscript{2} photonic diode.

To further estimate the \( n_2 \) of the photonic diode MoSe\textsubscript{2} and few other semiconducting materials from the nonreciprocal light propagation characteristics, similar experiments were performed. The similarity comparison method (SCM) allows us to estimate similarity contrast (\( S_C \)) of these materials using their nonlinear refractive indices \( n_2 \)\textsuperscript{[19]}

\[
S_C = 1 - D_C = 1 - \frac{n_{21} - n_{32}}{n_{32}} = 1 - \frac{\lambda}{2n_1 L_{\text{eff}}} \frac{d N_1}{d I_1} - \frac{\lambda}{2n_2 L_{\text{eff}}} \frac{d N_2}{d I_1} = 1 - \frac{N_1}{I_1} \frac{N_2}{I_2} = 1 - \frac{N_1}{I_1} \frac{N_2}{I_2} \tag{13}
\]

where \( D_C \) is the difference constant, \( n_{21} \) and \( n_{32} \) represent the nonlinear refractive index of the hybrid system obtained for the forward and reverse direction, respectively. The semiconducting Bi\textsubscript{2}Se\textsubscript{3}, CuPc, and graphene are used in combination with MoSe\textsubscript{2} for \( S_C \) studies which has been presented in Figure 5h–j and summary of the results is presented in Figure 5k. The \( S_C \) values for SnS\textsubscript{2}, CuPc, Bi\textsubscript{2}Se\textsubscript{3} and graphene are found to be 69\%, 75\%, 86\%, and 95\%, respectively. These results indicate that the MoSe\textsubscript{2} has similar nonlinear refractive index to the graphene\textsuperscript{[8,19,42,55]} Furthermore, the CuPc has very low \( S_C \) which is close to SnS\textsubscript{2} for \( \lambda = 405 \) nm.

\section*{2.5. Cross-Phase Modulation: MoSe\textsubscript{2}-Based All-Optical Switching and Logic Gates}

By taking advantage of the SSPM by MoSe\textsubscript{2} NFs, an all-optical switch has been demonstrated to perform the logical function like an OR gate as shown in Figure 6. The schematic of the experimental logical OR gate is presented in Figure 6a using the cross-phase modulation (XPM) technique\textsuperscript{[44,56]}. Two lasers with different wavelengths are used as the two input signals ("A" and "B") of the logic system on the MoSe\textsubscript{2} NFs based logic device. The resultant XPMs are the corresponding outputs of the logic gate. Figure 6b shows the symbol and switch circuit of the OR logic gate. Where the input "A" or "B" is in high-level "1", the output "Y" will also be in high-level "1", and only when both are at the lower level "0", the output will be low "0". The corresponding switching waveforms are ("A", "B", and "Y") presented in Figure 6c. Here, all the logic levels are realized by the number of diffraction rings formed using the XPM process. Here, we observed a two-laser-based system to achieve light–light modulation. The diffraction rings cannot be formed when the incident light or probe light is too low to interact with the sample, and in this case, only a Gaussian light appears on the screen. When another laser light (pump light) with relatively high intensity is cross-modulated with the Gaussian probe light, it can form diffraction rings on the screen for both the lights. The individual lights of \( \lambda = 532 \) and 671 nm are considered input "A" and input "B", respectively. Now both lights are cross-coupled, and the final image is formed on the screen, which is considered as the output "Y". Based on the output using two-lasers, we can build an optical logic OR gate, which is presented in Figure 6d–f for the combination of laser lights with \( \lambda = 532 \) and 671 nm, 405 and 532 nm, and 405 and 671 nm, respectively. Figure 6g presents the number of diffraction rings of the probe light (\( \lambda = 532 \) nm) with the intensity signal of the pump light \( \lambda = 671 \) nm, where the probe light intensities are 2.42, 3.06, and 4.08 W cm\textsuperscript{-2}, respectively. The initial number of diffraction rings formed by the probe light depends on the intensity of the probe light. The diffraction rings are modulated based on the superposition principle when the pump light is on. In addition, the diffraction ring numbers of the probe light linearly depend on the pump light’s intensity. For other two set of light combinations, \( \lambda = 405 \) and 532 nm, and 405 and 671 nm, the similar experiments are performed and presented in Figure 6g,i, respectively. Figure 6j–l shows the 3D model of the overall data obtained through the diffraction ring numbers of the probe light with the intensity of the pump and probe light for choice of pump and probe lights with \( \lambda = 532 \) and 671 nm, 405 and 532 nm, and 405 and 671 nm, respectively.

\section*{3. Conclusions}

In conclusion, we have reported the SSPM of Gaussian laser beams by suspended MoSe\textsubscript{2} NFs in a solvent. The NFs of 2D layered MoSe\textsubscript{2} are synthesized using a cost-effective solvothermal...
technique. The nonlinear broadband optical response of MoSe$_2$ NFs has been investigated using laser beams with $\lambda = 671$, 532, and 405 nm. The nonlinear refractive index and the monolayer third-order nonlinear susceptibility are estimated from the change in the diffraction ring number as a function of laser power. The obtained $n_2$ and $\chi^{(3)}$ for MoSe$_2$ NFs are found to be $1.3 \times 10^{-5}$ cm$^2$ W$^{-1}$ and $2.23 \times 10^{-8}$ esu, respectively at 532 nm excitation laser, are comparatively larger than other family members of TMDs. The large values of $n_2$ and $\chi^{(3)}$ reveal strong nonlinear coherent interaction of light with the ensemble of layered 2D MoSe$_2$ NFs. The evolution (formation) of the self-diffraction ring patterns due to SSPM have been

Figure 6. Cross-phase modulation: All-optical switching and logic gates. a) Schematic presentation of the XPM inside MoSe$_2$ NFs for photonic diode application. b) Symbol and circuit model of the logical OR gate. c) The waveform of OR gate (input: A and B; output: Y). d–f) MoSe$_2$ based experimental results for optical OR gate operation using two-color XPM technique for the combination of $\lambda = 532$ and 671 nm, 405 and 532 nm, and 405 and 671 nm, respectively. g–i) Change in the diffraction ring numbers of the probe lasers versus the intensity variation of the pump laser. j–l) 3D presentation of the two-color XPM for different pair of lasers ($\lambda = 532$ and 671 nm, 405 and 532 nm, and 405 and 671 nm).
described by the “wind-chime” model considering coherent light–matter interactions. Based on the SSPM, a passive photonic diode has been designed using MoSe$_2$/SnS$_2$ hybrid heterostructures to demonstrate the nonreciprocal light propagation. The unidirectional properties of the above photonic diode using MoSe$_2$ have been compared with a few other semiconducting materials (i.e., Bi$_2$Se$_3$, CuPc, and graphene) by the similarity comparison method. The all-optical switching properties have also been explored based on the two-color interband coherence. In addition, the all-optical information processing has been examined by performing the “OR” logic gate operation using cross-phase modulation (XPM) of two laser beams. We believe that these NLO phenomena can provide an inroad foundation for the MoSe$_2$ based all-optical switching as optical diodes and logic devices.

4. Experimental Section

Synthesis of MoSe$_2$ Nanoflakes: Facile solvothermal technique had been adapted to synthesize MoSe$_2$ NFs, and Figure 1a shows the schematic presentation of the synthesis process. The detailed preparation method of MoSe$_2$ NFs has been discussed in our earlier works.$^{[24,57]}$ In brief, a suitable amount of sodium molybdate (Na$_2$MoO$_4$·2H$_2$O) was added in 22.5 mL dimethylformamide (DMF) solution with 30 min sonication for proper dispersion at room temperature. Next, 15 mg of selenium powder was dispersed in 7.5 mL hydrazine hydrate by constant stirring in an oil bath at 80°C for 1 h. Then, this solution was mixed with the previously prepared DMF solution to maintain the atomic ratio of Mo:Se as 1:2. Then, the as-prepared solution was transferred into a 100 mL autoclave up to 60% of its volume and kept into an oven, which was already preheated at 180°C for 12 h. Thereafter, the autoclave was cooled down by natural cooling. Next, the obtained precipitate was filtered and washed by de-ionized water and ethanol multiple times. Finally, the black MoSe$_2$ powder was annealed at 450°C under N$_2$ atmosphere for 4 h to improve the crystallinity of MoSe$_2$ NFs.

Synthesis of SnS$_2$ Nanosheets: The synthesis process of SnS$_2$ had been done by following the process reported by Zhang et al.$^{[58]}$ Typically, 220 mg SnCl$_2$·5H$_2$O and 280 mg thioacetamide were mixed with 60 mL of de-ionized water and then transferred to a 100 mL Teflon-lined autoclave and the autoclave was heated and kept at 180°C for 24 h. After the reaction, the autoclave was allowed to cool naturally to room temperature, and the yellow-colored sample was collected after centrifuging the sample at 10 000 rpm. The final product was dried in a hot air oven at 80°C for 6 h and stored in a desiccator. The detailed characterization has been carried out and discussed in the Section S1, Supporting Information.

Characterization: Field-emission scanning electron microscopy (FESEM, Hitachi S-4800) and transmission electron microscopy (FEG-TEM) were used to characterize the sample morphology. Figure 1b,c shows the layered MoSe$_2$ NFs. Transmission electron microscopy−energy-dispersive X-ray spectroscopy spectrum and elemental mapping revealed the chemical composition and stoichiometric ratios of MoSe$_2$ NFs (see Figure 1d). The above analysis confirmed that the sample contained the elements Mo and Se with their atomic ratio about 1:2.07. Figure 1e shows the Raman spectrum of 2D MoSe$_2$ NFs with its characteristics in-plane (E$_g$, E$_g$) and out-of-plane (A$_{1g}$) vibrational modes. The high-resolution X-ray photoelectron spectroscopy showed the chemical environment of an element Mo 3d and Se 3d, which are presented in Figure 1f,g, respectively. The bandgap of the MoSe$_2$ NFs sample was determined to be $E_g = 1.6$ eV by the UV−vis absorption curve and corresponding Tauc plot curve as shown in Figure 1h. The characterized 2D layered MoSe$_2$ NFs had been dispersed in N-methyl-2-pyrrolidone (NMP) and a few other solvents (acetone, toluene, etc.) with different loading concentrations for the SSPM experiments.

Experimental Setup: The schematic of SSPM spectroscopy setup to study the NLO response of MoSe$_2$ NFs suspended in NMP solvent is shown in Figure 2a. The sample showed the broadband SSPM effect for the incident pump light with $\lambda = 671$, 532, and 405 nm, respectively. Here, the pump laser passed through a convex lens of 20 cm focal length ($f$) and incident on a quartz cuvette of thickness 10 mm, which was placed near the focal point of the lens. Under intense coherent Gaussian laser beam, the suspended MoSe$_2$ NFs interacted with the incident laser and the MoSe$_2$ NFs started to orient along the optical electric field.$^{[59]}$

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

all-optical logic gates, all-optical modulation, Kerr nonlinearity, MoSe$_2$, spatial self-phase modulation

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