

Ultrafast large third-order optical nonlinearity in titanium carbide MXene-VS₂ hybrids

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The ultrafast nonlinear optical responses of materials are not just theoretical concepts, but they play a significant role in developing modern photonic and optoelectronic devices, including optical time crystals. However, conventional materials often display either weak optical nonlinearities or slow response in the nanosecond timescale, rendering them ineffective for single-shot femtosecond pulse. This limitation can be overcome by leveraging the ultrafast charge transfer that is less than or equal to the pulse width of the laser in a donor-acceptor material pair. However, the low charge-transfer rates limit their effectiveness in high-speed applications. Here, we synthesized titanium carbide MXene-VS₂ hybrids characterized by strong electronic coupling, resulting in a remarkable enhancement in the ultrafast third-order nonlinear optical responses, enabled by charge transfer in less than the pulse width. For instance, we obtained a third-order nonlinear optical absorption coefficient of $(150 \pm 16) \times 10^{-3}$ cm/GW and a self-focusing (positive) nonlinear refractive index of $(94 \pm 9) \times 10^{-6}$ cm²/GW at 800 nm in the femtosecond domain, both exceeding control samples by more than an order of magnitude. These enhancements are attributed to efficient charge transfer within the hybrid structure, supported by first-principles calculations and Bader charge analysis. Our findings have led to the development of an ultrafast optical limiter, featuring an onset threshold as low as 0.60 ± 0.05 mJ/cm², with a differential limiting transmittance of 0.46 ± 0.02 . These parameters are better than or comparable to the known benchmarks for high-speed nonlinear optical applications, demonstrating the potential for advanced photonic and optoelectronic devices.

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I. INTRODUCTION

Recent advances in ultrafast nonlinear optical responses are critical for photonic and optoelectronic devices [1,2], including optical limiters [3,4], optical time crystals [5–7], and ultrafast

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modulators [8–10]. Optical limiters are materials or devices designed to protect sensitive eyes, sensors, and optical components from laser-induced damage by transmitting low-intensity light with minimal attenuation, while strongly suppressing high-intensity light once the input surpasses a threshold. This protective functionality is widely used in quantum information processing [11,12], soliton generation [13], pulse shaping [14,15], and biomedical applications [16]. All these applications require a very large and fast nonlinear optical response. With that demand, a variety of material systems are explored by exploiting the natural nonlinear response and typical examples are quantum wells [17], plasmonic metals [18], epsilon-near-zero materials [19,20], graphene oxide (GO) [3], black phosphorus [21], fullerenes [22], carbon nanotubes (CNTs) [23], inorganic-organic halide perovskites [24], transition metal dichalcogenides (TMDs) [25,26], transition metal oxides [27,28], amorphous chalcogenide films [29], etc. However, the intrinsic nonlinear optical responses in most materials are typically weak due to their perturbative nature [30]. It has been demonstrated that the intrinsic nonlinearity of a material can be markedly enhanced through charge transfer by creating hybrids of charge-donating and charge-accepting materials [3]. Such hybrid systems offer a promising approach to overcome these limitations. For example, enhanced nonlinear optical responses have been reported in VSe₂-rGO [31] and single-walled CNT-VSe₂ nanohybrids [32], where the nonlinearity is ~ 10 times larger than that of their controls. Other hybrid materials, such as MoSe₂/GO [33], hybrids of gold nanoparticles with CdSe [34], WS₂ [35], and Ge₂₄Se₇₆ [29], graphene/MoS₂ [36], and Cs₄PbBr₆/WS₂ [24], have also shown improved nonlinear optical responses. However, responses of most of these hybrids are limited to picosecond (ps) or nanosecond (ns) timescales due to slow charge-transfer rates [3,24]. While ns-ps devices are fast and suitable for many continuous-wave or long-pulse scenarios, they cannot clamp within a single femtosecond (fs) pulse. For single-shot protection against ~ 50 – 300 fs pulses, the characteristic response time (τ) must be less than or equal to pulse width. This distinction matters because damage can occur within a single fs pulse, so a limiter responding on ns-ps scales primarily does not protect against intra-fs pulse damage. Consequently, the identification of donor-acceptor hybrid materials capable of operating in fs pulse regimes with ultrafast charge-transfer rates remains a critical challenge, which has pushed the exploration of unique or previously overlooked material systems, including quantum wells [17].

One plausible way to tackle this issue could be by creating donor-acceptor hybrid structures of Ti₃C₂T_x (MXene) and VS₂, where T_x denotes surface terminations such as hydroxyl (–OH), oxygen (=O), and fluorine (–F) [37]. Our motivation behind selecting this hybrid is due to (1) MXene, a family of layered material [38,39], and (2) among the TMDs, VS₂ stands out due to its excellent potential as a nonlinear optical material exploiting its large chemically active surface area and extreme mechanical strength inherent in its two-dimensional structure [37,40]. Individually, MXenes and VS₂ exhibit beneficial nonlinear optical properties with lower magnitudes [41,42]. Thus, incorporating VS₂ with MXene presents an effective strategy to enhance third-order optical nonlinearity and device performance through charge-transfer mechanisms. Recent research has indicated effective charge transfer in MXene-VS₂ hybrids, suggesting their promise for energy storage and gas-sensing applications [37,43]. Despite these advances, active control of ultrafast third-order optical nonlinearity mediated by charge transfer remains largely unexplored.

Here, we report a manifold enhancement in the excited-state absorption (ESA) coefficient (β) and nonlinear refractive index (n_2) of the MXene-VS₂ hybrid at 800 nm, 120 fs pulsed excitation compared to control materials that show only saturable absorption (SA) and negative n_2 within the fs regime. For instance, we demonstrate β of $(150 \pm 16) \times 10^{-3}$ cm/GW and an n_2 of $(94 \pm 9) \times 10^{-6}$ cm²/GW, which exceed control samples by at least an order of magnitude. This significant enhancement of the real and imaginary parts of the third-order optical susceptibility is attributed to the ultrafast charge transfer between MXene and VS₂. First-principles calculations and Bader charge analysis reveal strong electronic coupling in the hybrid, with electron transfer from MXene to VS₂. Exploiting the strong ESA of our hybrid system, we have successfully fabricated a high-performance ultrafast optical limiter, exhibiting key device parameters such as an onset threshold

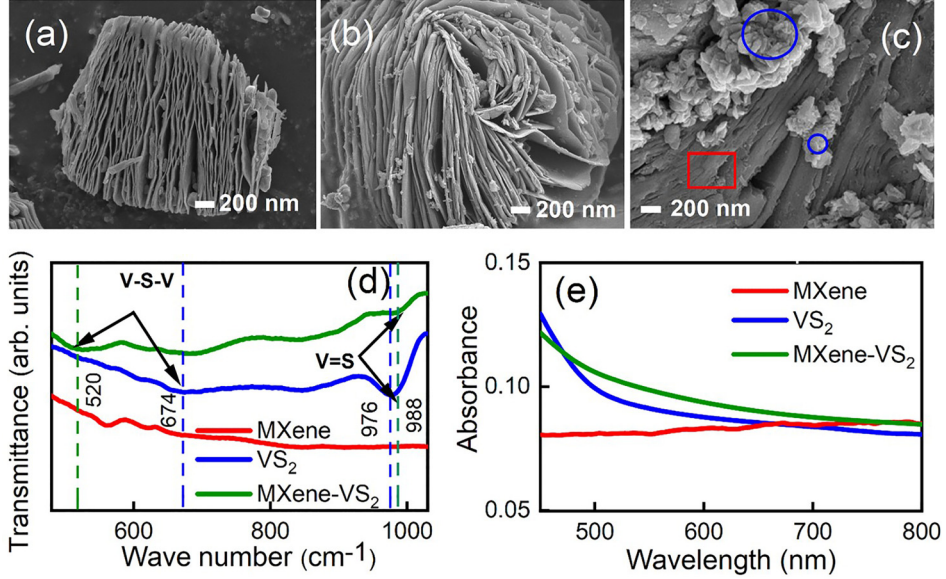


FIG. 1. High-magnification FE-SEM images of (a) MXene, (b) VS₂ nanosheets, and (c) MXene-VS₂ hybrid; in the figure, blue circle and red rectangle represent the regime of VS₂ and MXene in the hybrid, respectively, showing the distinct morphologies of each sample. (d) FTIR spectra of VS₂, MXene, and the MXene-VS₂ hybrid, highlighting the shifts in vibrational modes indicative of strong interactions between MXene and VS₂. (e) UV-Vis absorption spectra of MXene (red line), VS₂ (blue line), and the MXene-VS₂ hybrid (green line) highlight the distinct absorption features of each component and the redshift observed in the MXene-VS₂ hybrid due to electronic coupling.

(F_{ON}) of 0.60 ± 0.05 mJ/cm² and a limiting differential transmittance (T'_{diff}) of 0.46 ± 0.02 . These results surpass the performance of several benchmark optical limiters operating in the fs regime.

II. SAMPLE CHARACTERIZATION

We have synthesized high-quality VS₂ nanosheets and strongly coupled MXene (Ti₃C₂T_x)-VS₂ hybrid by using the hydrothermal method and MXene by the minimally intensive layer delamination method [44]. The synthesis process is schematically outlined in Fig. S1 of the Supplemental Material [45]; for details, see Sec. S1 of the Supplemental Material [45]. The successful formation of strongly coupled MXene-VS₂ hybrids is confirmed through the powder x-ray diffraction (PXRD) pattern shown in Fig. S2 of the Supplemental Material [45]. Notably, a shift in the Bragg peak from $\sim 8.7^\circ$ to 6.9° , along with the emergence of a broad peak at $\sim 27.9^\circ$, absent in the control samples, confirms the formation of hybrid structures. The morphologies of the synthesized samples were characterized by field emission scanning electron microscopy (FE-SEM). Figures 1(a) and 1(b) show the FE-SEM images of VS₂ and MXene, which exhibit layered sheetlike morphology and etched layers, respectively. Figure 1(c) shows the FE-SEM image of the MXene-VS₂ hybrid, where VS₂ sheets disintegrate into smaller fragments that assemble on or between the MXene flakes, effectively preventing the restacking of an effect not observed in the control VS₂ samples.

The strong interaction between VS₂ nanosheets and MXene layers in the hybrid structures is confirmed by Fourier transform infrared (FTIR) spectroscopy [Fig. 1(d)]. The S-V-S band within the hybrid shifts from 674 to 520 cm⁻¹ and the V=S band shifts from 976 to 988 cm⁻¹, with both bands broadening. The observed shift in the bending vibrations of the S-V-S and V=S bands in the MXene-VS₂ hybrid indicates the strong interaction between the MXene functional groups and the doubly bridged S²⁻ species [42,46]. Further, the Raman spectrum of the MXene-VS₂

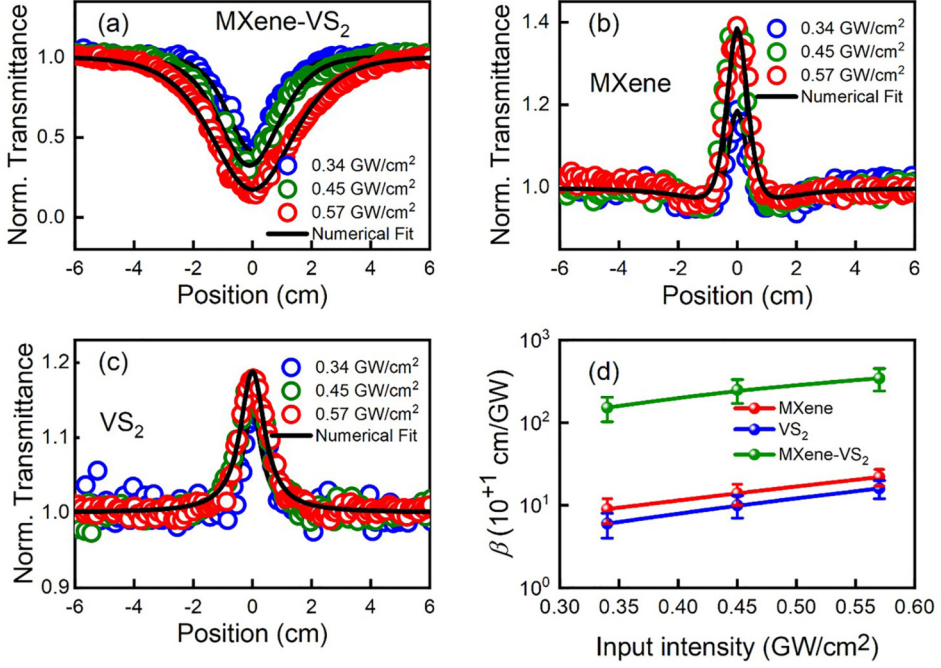


FIG. 2. Open-aperture Z-scan traces measured at 800 nm for (a) MXene-VS₂ hybrid, (b) MXene, and (c) VS₂ nanosheets at varying on-axis peak intensities, illustrating the distinct nonlinear optical responses, ESA in the MXene-VS₂ hybrid, and SA in MXene and VS₂. (d) Variation of β with input intensity for MXene-VS₂ hybrid, MXene, and VS₂.

hybrid shows a combination of signals from the control samples, with a prominent blueshift of the characteristic peak from 510 cm^{-1} in MXene to 525 cm^{-1} in the hybrid; see Fig. S3 in the Supplemental Material [45]. This shift provides further evidence of strong electronic coupling between VS₂ and MXene in the hybrid. Figure 1(e) presents the UV-Vis absorption spectra of MXene (red line), VS₂ nanosheets (blue line), and the MXene-VS₂ hybrid (green line). MXene shows a relatively flat absorption across the visible region, consistent with its metallic nature as previously reported [41,47]. In contrast, VS₂ exhibits an absorption onset of around 530 nm. In the MXene-VS₂, the absorption spectrum integrates characteristics of both MXene and VS₂, with the absorption features of VS₂ with a pronounced redshift. This behavior indicates strong electronic coupling and efficient charge transfer between MXene and VS₂ in the hybrid [31,32].

III. RESULTS AND DISCUSSION

To investigate the third-order nonlinear optical responses of MXene-VS₂, MXene, and VS₂ samples, we employed the open-aperture Z scan, which quantifies the total transmittance as a function of incident laser intensity [27,48,49]. For this, we employed 120 fs, 800 nm laser pulses generated from Ti:sapphire to excite our sample in a standard quartz cuvette having path length of 1 mm. The repetition rate of the incident laser was 1 kHz. More details about the experiments are provided in Sec. S2 and Fig. S4 of the Supplemental Material [45]. For the measurement, all the samples have been diluted in distilled water with a linear transmittance of 60% and 0.5 mg/ml concentration. To rule out any influence of the cuvette or solvent, we performed Z-scan measurements of solvent in the same cuvette at intensities up to 200 GW/cm^2 ; for details, see Fig. S5 and Sec. S2 of the Supplemental Material [45]. Figure 2(a) shows the Z-scan traces for the MXene-VS₂ hybrid at 800 nm, using a peak intensity of 90 GW/cm^2 at the focal point. Notably, the Z-scan

TABLE I. The calculated σ_{GS} and σ_{ES} for MXene, VS_2 , and MXene- VS_2 hybrid at 800 nm excitation.

Sample	Intensity	σ_{GS}	σ_{ES}
MXene	30	1.5 ± 0.2	0.7 ± 0.1
	90	2.2 ± 0.4	1.1 ± 0.2
	150	3.5 ± 0.5	1.6 ± 0.4
VS_2	30	1.0 ± 0.2	0.5 ± 0.1
	90	1.6 ± 0.4	0.9 ± 0.3
	150	2.4 ± 0.6	1.5 ± 0.4
MXene- VS_2	30	2.5 ± 0.6	6.0 ± 0.9
	90	3.8 ± 1.0	8.6 ± 1.5
	150	5.4 ± 1.2	15.0 ± 2.0

traces of the sample exhibit a distinct reduction in transmission as the sample approaches the focal point, a behavior indicative of nonlinear absorption. The experimental data were analyzed using nonlinear absorption models (detailed in Sec. S2 of the Supplemental Material [45]), providing β of $(150 \pm 16) \times 10^{-3}$ cm/GW, along with the saturation intensity (I_0) of $(6.1 \pm 0.5) \times 10^{-2}$ GW/cm². To further understand the mechanism, we performed intensity-dependent Z-scan measurements. Figure 2(d) demonstrates that the β values have monotonic increase with peak intensity, indicating that the nonlinear optical response originates from ESA, as opposed to the two-photon absorption, where a constant β would be expected. In further support of the ESA mechanism, we calculated the excited-state (σ_{ES}) and ground-state (σ_{GS}) absorption cross sections [50] (details are provided in the Supplemental Material [45]). The analysis revealed that the values of σ_{ES} exceed σ_{GS} , as presented in Table I. This result validates the occurrence of ESA in the MXene- VS_2 hybrid [32].

In stark contrast to the MXene- VS_2 hybrid, the Z-scan traces of MXene show an increase in transmittance as the sample moves toward the focal point, reaching a maximum at the focus, which is characteristic of SA [51] [Fig. 2(b)]. This behavior can be understood by considering the fact that, at this intensity, ground-state carriers are depleted, leading to a condition where $\sigma_{ES} < \sigma_{GS}$, a key criterion for observing SA [3,32,50,52]. The Z-scan traces for VS_2 exhibit a similar SA response shown in Fig. 2(c). This behavior in VS_2 can be explained by band structure modulation due to defect states, such as vanadium or sulfur vacancies, or the coexistence of both semiconducting and metallic phases. These defects introduce sub-bandgap states, which can easily saturate due to their low density and show SA when excited at 800 nm. Our calculations further support this explanation, showing that for VS_2 $\sigma_{ES} < \sigma_{GS}$ (see Table I) confirms the SA behavior through sub-bandgap absorption mediated by defect states. Our results demonstrate that the integration of electron-donating MXene with VS_2 can induce ESA in the hybrid, a significant departure from the SA observed in the control materials. This unprecedented nonlinear optical response in the MXene- VS_2 hybrid is driven by efficient ultrafast charge transfer less than or equal to pulse width, marking an approach for single-shot protection against ~ 50 –300 fs pulses.

After observing the enhanced imaginary part of the third-order nonlinear optical response in the MXene- VS_2 hybrid, we investigated the effect of charge transfer on the real part— n_2 . The sign and magnitude of n_2 were determined using the closed-aperture Z-scan technique, with an aperture positioned before the detector to reduce transmission to one-third of the input laser intensity [27,48,49]. Figures 3(a)–3(c) present the closed-aperture Z-scan results for the MXene- VS_2 and controls (MXene and VS_2) at various on-axis peak intensities. Notably, the MXene- VS_2 hybrid displays a valley-to-peak pattern, indicative of a self-focusing effect that corresponds to positive nonlinearity ($\text{Re } \chi^{(3)} > 0$) [48]. In contrast, the control MXene and VS_2 samples exhibit the typical peak-to-valley pattern, which is characteristic of a self-defocusing effect associated with

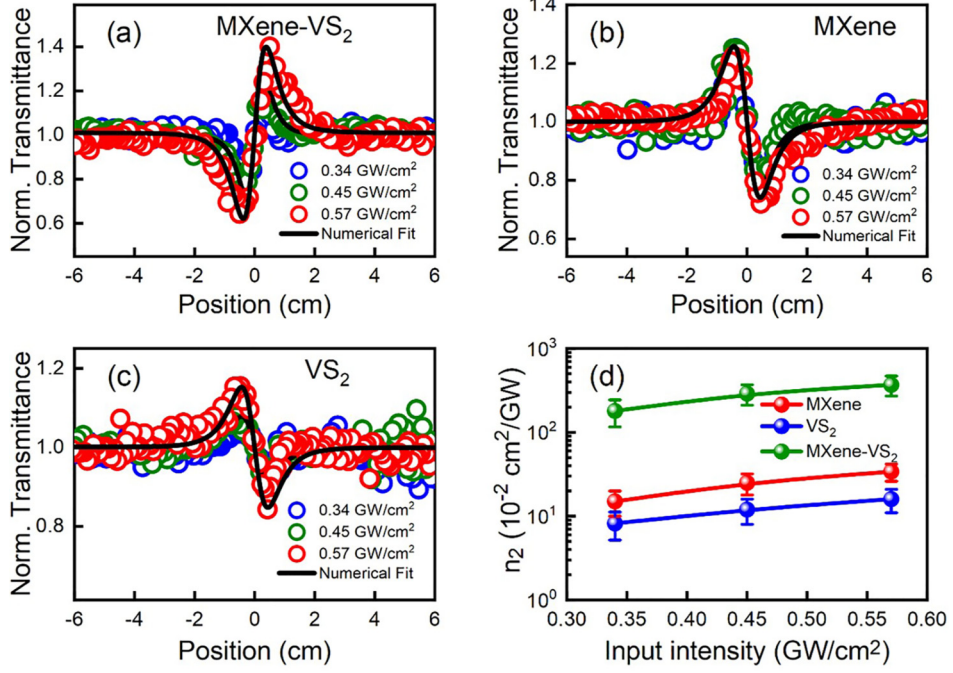


FIG. 3. Closed-aperture Z-scan traces measured at 800 nm for (a) MXene-VS₂ hybrid, (b) MXene, and (c) VS₂ nanosheets at varying on-axis peak intensities, illustrating the distinct nonlinear optical responses: self-focusing (positive nonlinearity) in the MXene-VS₂ hybrid and self-defocusing (negative nonlinearity) in MXene and VS₂. (d) Variation of n_2 with input intensity for MXene-VS₂ hybrid, MXene, and VS₂.

negative nonlinearity ($\text{Re } \chi^{(3)} < 0$); further details are provided in Sec. S4 of the Supplemental Material [45,53].

To quantify these observations, we modeled the closed-aperture Z-scan traces using Eq. (S6) [45,54–56]; details are provided in Sec. S2 of the Supplemental Material [45]. The extracted n_2 values are provided in Table II; for example, MXene-VS₂ shows $n_2 = (94 \pm 9) \times 10^{-6} \text{ cm}^2/\text{GW}$ at on-axis peak intensity of 90 GW/cm², which is an order of magnitude larger than $(8 \pm 0.7) \times$

TABLE II. Third-order nonlinear parameters: ESA coefficient (β) and refractive index (n_2) at 800 nm excitation with different peak intensities.

Sample	Intensity	$\beta \times 10^{-3}$	$n_2 \times 10^{-6}$
MXene	30	$-(3.0 \pm 0.4)$	$-(6.0 \pm 0.4)$
	90	$-(5.0 \pm 0.6)$	$-(8.0 \pm 0.7)$
	150	$-(8.0 \pm 0.8)$	$-(10.0 \pm 1.0)$
VS ₂	30	$-(4.0 \pm 0.2)$	$-(4.0 \pm 0.3)$
	90	$-(8.0 \pm 0.5)$	$-(5.0 \pm 0.4)$
	150	$-(12 \pm 1)$	$-(7.0 \pm 0.5)$
MXene-VS ₂	30	78 ± 6	76 ± 8
	90	150 ± 16	94 ± 9
	150	225 ± 35	130 ± 22

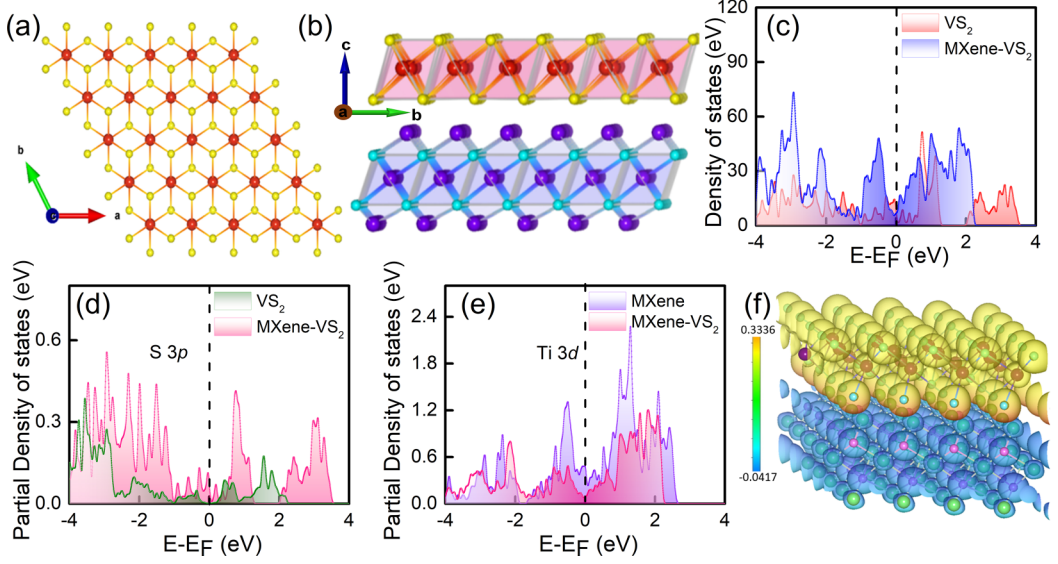


FIG. 4. Optimized structure of (001) plane for (a) VS_2 and (b) MXene-VS_2 hybrid. Yellow, red, cyan, and violet indicate S, V, C, and Ti atoms, respectively. (c) TDOS for VS_2 and MXene-VS_2 hybrid, (d) PDOS for S 3p orbital of VS_2 and MXene-VS_2 hybrid, and (e) PDOS for Ti 3d orbital of MXene and MXene-VS_2 hybrid. (f) The charge density picture illustrates the difference in charge between MXene and hybrid with an iso-value of 0.07e. The yellow region represents VS_2 gaining charge, while the blue region represents MXene losing charge.

$10^{-6} \text{ cm}^2/\text{GW}$ for MXene and $(5 \pm 0.4) \times 10^{-6} \text{ cm}^2/\text{GW}$ for VS_2 . Further, the n_2 values shown in Fig. 3(d) display a monotonic increase with peak intensity. Moreover, we completely characterize the third-order nonlinear susceptibility ($\chi^{(3)}$) using the following equation [50,57,58]:

$$\chi^{(3)} = \chi_R^{(3)} + i\chi_I^{(3)}, \quad (1)$$

where $\chi_R^{(3)}$ and $\chi_I^{(3)}$ are, respectively, the real and imaginary parts of the nonlinear optical susceptibility; details are provided in Sec. S4 of the Supplemental Material [45] and values of $\chi^{(3)}$ are provided in Table S3 of the Supplemental Material [45].

The fs Z-scan measurements reveal ultrafast charge transfer in MXene-VS_2 hybrid. With this logic, we extended the pulse width of the laser by up to 7 ns (excitation wavelength = 532 nm) by employing ns open- and closed-aperture Z-scan measurements; see Sec. S6 of the Supplemental Material [45]. The result reveals that the charge transfer becomes more efficient and the values of β and n_2 are $(250 \pm 80) \times 10^1 \text{ cm/GW}$ and $(290 \pm 80) \times 10^{-2} \text{ cm}^2/\text{GW}$, respectively, showing four orders of magnitude enhancement as compared to the fs excitation.

To theoretically investigate the charge transfer mechanism, we performed first-principles density functional theory calculations using VASP [59–64]; further details are provided in Sec. S5 of the Supplemental Material [45]. For the MXene-VS_2 hybrid, we modeled the system with a monolayer corresponding to the (002) plane of MXene from the MAX phase. The optimized structures of the VS_2 monolayer and the MXene-VS_2 hybrid (001) plane are presented in Figs. 4(a) and 4(b). The MXene-VS_2 hybrid comprises two layers: a 3×3 supercell of VS_2 under periodic boundary conditions, positioned $3.5 \text{ \AA}$ above a 3×3 MXene layer.

To understand the hybridization effect between MXene and VS_2 , we computed the total density of states (TDOS) for the VS_2 (001) monolayer and the MXene-VS_2 hybrid [Fig. 4(c)]. The TDOS reveals an enhancement in the states across the entire valence band due to MXene addition to VS_2 . For a more detailed analysis of orbital interaction and charge contribution after hybridization, we

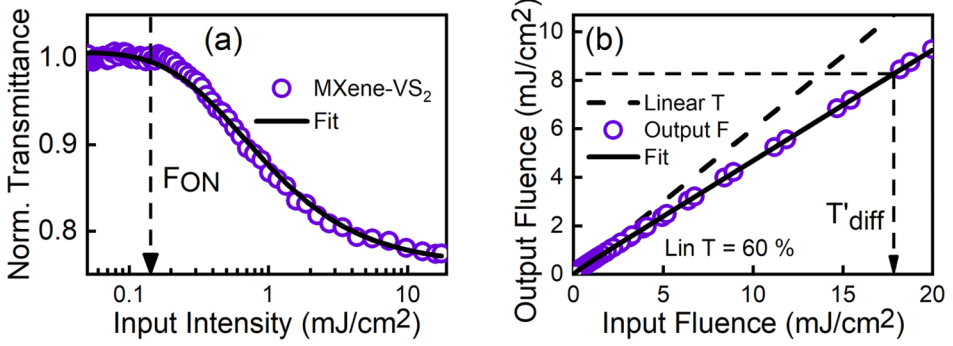


FIG. 5. (a) Normalized transmittance vs input intensity. (b) Output fluence vs input fluence.

plotted the partial density of states (PDOS) for the S $3p$ orbital of VS₂ and the Ti $3d$ orbital of MXene [Figs. 4(d) and 4(e)]. After hybridization, the S $3p$ orbital shows a sharp increase in states below the Fermi level, while the Ti $3d$ orbital exhibits an overall decrease in states in the hybrid system.

To quantitatively confirm the charge transfer, we conducted Bader charge partitioning [65]. The Bader charge analysis shows that for the MXene-VS₂ hybrid, there is a transfer of 6.8e charge from MXene to VS₂ in the supercell containing 72 atoms (27 atoms for VS₂ and 45 atoms for MXene), consistent with the PDOS analysis. To account for individual atoms that are interacting between two surfaces, S $3p$ and V $3d$ orbitals gain 0.73e and 0.07e charge, respectively, from the MXene, while Ti $3d$ and C $2p$ orbitals lose 0.34e and 0.007e to VS₂. To further visualize the charge transfer, Fig. 4(f) presents the charge density difference between the MXene-VS₂ hybrid and control MXene. The yellow regions represent VS₂ gaining charge, while the blue regions show MXene losing charge. This visualization clearly demonstrates electron transfer from MXene to VS₂ in the hybrid, validating the charge transfer mechanism.

The MXene-VS₂ hybrid exhibits a notable enhancement in both β and n_2 , emphasizing its potential as a high-performance ultrafast optical limiter. Two key metrics define its optical limiting performance: (1) onset threshold fluence (F_{ON}), the fluence at which normalized transmittance begins to deviate from linearity, marking the initiation of optical limiting and (2) limiting differential transmittance T'_{diff} (dI_{out}/dI_{in}), which quantifies the material's ability to attenuate transmitted light as fluence increases in the nonlinear regime [32]. A superior optical limiter requires both low F_{ON} and T'_{diff} values. The MXene-VS₂ hybrid achieves a low F_{ON} of 0.60 ± 0.05 mJ/cm² and a T'_{diff} of 0.46 ± 0.02 [see Figs. 5(a) and 5(b)]; these parameters are better than or comparable to the known benchmark materials, as tabulated in Table III. These low F_{ON} and T'_{diff} values highlight the MXene-VS₂ hybrid's promise for next-generation optical limiting applications, offering a powerful combination of speed, efficiency, and material versatility.

TABLE III. Onset F_{ON} and differential transmittance T'_{diff} are compared to those of various benchmark optical limiters.

System	Wavelength (nm)	Lin T	F_{ON} (mJ/cm²)	T'_{diff}	Reference
MXene-VS ₂	800	60	0.5	0.46	Present work
SWCNT/VSe ₂	800	70	4	0.54	[32]
SWCNT/VSe ₂	900	66	3	0.53	[32]
Au NP-rGO	532	70	50	0.3	[3]
SiO ₂ -Se	800	85	54		[66]

IV. CONCLUSION

In summary, we have demonstrated that the ultrafast third-order nonlinear optical response, encompassing both real and imaginary components, can be significantly enhanced by at least an order of magnitude through charge transfer in MXene-VS₂ hybrids compared to their controls. Notably, the imaginary part of the nonlinear response in the MXene-VS₂ hybrid exhibited unprecedented ESA with a β value of $(150 \pm 16) \times 10^{-3}$ cm/GW, a marked difference over the SA observed in control MXene and VS₂. Moreover, the real part of the nonlinear response in the hybrid showed a self-focusing effect with an n_2 value of $(94 \pm 9) \times 10^{-6}$ cm²/GW, in stark contrast to the self-defocusing behavior in the control, driven by ultrafast charge transfer. First-principles calculations, supported by Bader charge analysis, confirmed robust electronic coupling between MXene and VS₂, with significant electron transfer from MXene to VS₂. Given that MXene-VS₂ is already established as a high-performance supercapacitor, we successfully engineered an optical limiting device with very low F_{ON} and T'_{diff} , emphasizing the hybrid's potential for next-generation optical limiting applications. These findings offer valuable insights into the manipulation of nonlinear optical properties, paving the way for the development of advanced all-optical photonic devices for optical limiting and switching.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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