Flexible Broadband Terahertz Modulation Based on Strain-Sensitive MXene Material

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A flexible broadband terahertz modulator based on a strain-sensitive MXene material is reported. MXene is shown to have high terahertz wave absorption through experimental testing of various substrate samples. Results show that the THz signal transmission increases with increasing stretching degree, which differs obviously from transmission through pure PVAc substrates. Analysis of the terahertz time-domain spectrum and electrical characterization indicate that the sample’s conductivity decreases with increasing stretching degree. The trend and magnitude of the electrical conductivity results are also very similar to those from the time-domain spectrum. MXene is shown to be a simple, efficient terahertz broadband spectrum modulator with transmittance that can be affected by applying external forces.

Keywords: terahertz modulation, MXene, strain-sensitive, flexible, broadband

INTRODUCTION

As a unique radiation wave type, terahertz waves have had a profound impact on fields including molecular biology, medical imaging, security detection and future communication systems [1–5]. The terahertz wave modulator is the core component of terahertz wireless communications, high-speed data transmission and high-resolution imaging systems. This modulator has characteristics that include low energy requirements, low transients, broadband performance, high coherence and strong perspective properties. In recent years, increasing numbers of different terahertz modulator types have been proposed. The functions of terahertz devices (including modulators [6–11], filters [12], polarizers [13, 14] and metamaterials [15–19]) are critical to the acceleration of spectral, imaging and communications applications using terahertz technology. In recent years, various methods for fabrication of high-efficiency THz modulators have been proposed, including fabrication of an in-band transition using graphene-induced perturbation, phase changes using vanadium dioxide (VO2), formation of composite metamaterials using split ring resonators and silicon light excitation. Although considerable efforts have been made to design and optimize the THz wave dynamic tuning materials, these efforts have been hindered by the low tuning efficiency of these materials. Therefore, the efforts to develop new terahertz modulation materials with high efficiency are of major significance. In recent years, flexible optoelectronic devices have attracted widespread attention because they can operate under various mechanical deformation conditions to meet the requirements of wearable or flexible applications [20–24]. For example, in 2018, Zhang et al. reported an engineering three-dimensional integrated framework for grinding stretchable electronic products by combining material design with advanced micromachining strategies [20]. At the same
time, some research on flexible terahertz devices was proposed [25–27], but most of the research focused on the integration of device units with flexible substrates. For example, Suzuki et al. designed terahertz metal cells that contained carbon nanotubes (CNTs) to form a flexible terahertz scanner and demonstrated the potential of this scanner in imaging of three-dimensional curvature objects [26]. Cong et al. fabricated a THz metamaterial quarter-wave plate composed of a metal wire grid layer and an isotropic polyimide layer that can be bent to cover a detector and used to explore the chirality of biomacromolecules [27]. However, these functions are essentially dependent on the nature of the device unit and must be performed using metamaterials with complex structures. In 2020, Shi et al. developed a flexible terahertz modulation method based on conductive polymer composites composed of thermoplastic polyurethane (TPU) and conductive Ni particles. This flexible layer exhibits the resistivity change of six to seven orders under tensile strain, which can be used to control the THz transmission with a giant modulation depth as high as 96%. Starting from the structural role of metamaterials, THz radiation can be modulated flexibly using the properties of materials [28]. Therefore, flexible material modulators with simple structures and obvious effects are desirable.

MXenes represent a new family of two-dimensional transition metal carbides and nitrides with the general formula $M_{n+1}X_nTx$ where $M$ is an early transition metal (Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, etc.), $X$ is carbon or nitrogen, and $Tx$ represents surface terminations, (e.g. hydroxyl, oxygen, or fluoride terminations) [38, 39]. MXenes have attracted major interest because of their interesting and diverse mechanical, structural, physical and chemical properties. Most importantly, MXenes exhibit ultra-high conductivity (1500 S/cm) on hydrophilic surfaces [29]. Because of this unique characteristic, MXenes have attracted extensive attention in fields such as energy storage [30–32], selective ion screening [33, 34], intelligent materials [35], electromagnetic interference shielding [36], and lasers [37]. Current research indicates that MXenes show excellent responses to electromagnetic waves. Jhon reported that Ti$_x$C$_2$ has high absorption and extinction coefficients in the terahertz range based on a first principles study [38]. This type of material with its strong absorption properties has drawn our interest strongly and we have previously fabricated a flexible broadband terahertz modulator based on a strain-sensitive MXene material.

In this work, the terahertz signal absorption of an MXene [Ti$_x$C$_2$T$_x$(T$_x$ = −OH, −O)]/PVAc(latex) sample is obviously reduced under the application of external tension, and the terahertz wave is thus modulated effectively to a large extent. During the material stretching process, the conductivity of the sample decreases as the degree of stretching increases, which results in increased THz wave transmission. The THz modulator introduced in this paper has advantages that include a simple structure, simple implementation and an obvious effect.

**EXPERIMENTAL DETAILS**

The substrate was fixed on a clean quartz wafer, then a thin MXene dispersion layer was spin coated on a clean emulsion substrate (1.5 cm × 3 cm × 0.2 mm), and sintered at 100°C for 15 min. Subsequently, silver parallel electrodes (1 cm long × 0.5 cm wide × 200 nm thick, with a distance between the electrodes of 5 mm) are deposited on the MXene layer by thermal evaporation in a vacuum chamber. Finally, a silver glue layer is coated onto the silver electrode and sintered at 100°C for 15 min. The sample is then removed from the quartz sheet and fixed onto a stretchable sample holder.

By performing scanning electron microscopy (SEM) surface morphology tests, we obtained the surface morphologies of the samples in the relaxed and flat state and the tensile state. The SEM surface topography of the MXene[Ti$_x$C$_2$T$_x$(T$_x$ = −OH, −O)]/PVAc(latex) sample are shown in Figures 1B,C. Figure 1C shows the morphology of the surface and section of MXene sample in the non-tensile state (the small picture in the upper right corner is a sectional view). Figure 1C shows the surface morphology of mxene under tension. As shown in Figures 1B,C, when the magnification is 35,000 times, we can see that the surface under tension is less wrinkled and much smoother than that in the relaxed state.

A GaAs photoconductive antenna was used to generate terahertz pulses with bandwidths in the 0.2–1.2 THz range. To detect the transmitted terahertz signals, a ZnTe crystal was used with an electro-optical sampling technique. The electro-optic effect is basically a nonlinear coupling effect between a low-frequency electric field (the terahertz pulse) and an optical pulse in the sensor crystal (ZnTe). The modulation of the polarization ellipticity of an optical probe beam that passes through the ZnTe crystal caused by modulation of the ZnTe crystal’s birefringence by a terahertz pulse is analyzed to gain information on both the amplitude and the phase of the terahertz wave. The tensile sample holder with the sample is placed into a THz time-domain spectroscopy (THz-TDS) system and the terahertz light spot is aimed at the titanium carbide part of the holder between the electrodes, as shown in Figure 1A. By adjusting the knob on the left side of the sample holder to adjust the stretching degree of the sample, the terahertz time-domain spectra of terahertz transmission characteristics of different stretched samples are obtained. The corresponding frequency spectrum can be obtained by applying a Fourier transform, and the conductivities of the samples with different tensile degrees can be calculated using the method described in Formula 2. The reference value is taken from the tensile data of an uncoated titanium carbide substrate.

The procedure is described as follows. First, connect the two ends of the sample via the electrodes to the source meter, and take the relaxed and flat state of the sample as the initial state; stretch the sample by a stretching amount of 5.7%, which acts as the change unit, and apply voltages ranging from 1V to −1V; collect the current information at 10 points, obtain the current-voltage (I-V) diagram for different stretching degrees, and then calculate the resistance value and conductivity of the sample.

**RESULTS AND DISCUSSION**

The terahertz time domain spectra of PVAc samples with and without MXene coatings are shown in Figure 2A. The sample
FIGURE 1 | (A) Schematic of the experimental setup. (B) Surface morphology of the sample without tension. (C) Surface morphology of the sample under tension.

FIGURE 2 | (A) Terahertz time-domain spectra of samples with and without MXene coating on PVAc substrates. (B) Terahertz frequency-domain spectra of samples with and without MXene coating on PVAc substrates. (C) Terahertz time-domain spectra of samples with and without MXene coating on sponge substrates. (D) Terahertz frequency-domain spectra of samples with and without MXene coating on sponge substrate.
that was coated with MXene reduced the transmission peak of the THz wave by approximately 80%. As shown in Figure 2B, the transmission frequency spectrum of the terahertz wave shows a major transmission difference before and after spin coating of the MXene material. This shows that the MXene has a very high absorbing capacity. At the same time, a sponge material was also used as a sample substrate in an additional experiment, with results as shown in Figures 2C,D. The results obtained are similar to those for the PVAc substrate.

The tensile results for the PVAc substrate are shown in Figure 3A. These results show that the substrate self-stretching has little effect on the THz transmission. Figure 3B shows the terahertz transmission power spectrum of the PVAc under tension. When the substrate is stretched, the THz signal decreases slightly. The time-domain spectra of the MXene/PVAc structure are studied under different tensile degrees, with results as shown in Figure 3C. All the tensile percentages in this paper are calculated by the ratio of the length after stretching to the original length. When the degree of stretching is 136%, the transmission amplitude of the time-domain spectrum increases by more than 42%. When the tensile strength is 147%, the transmission amplitude then increases by more than 63%. When the tensile strength reaches 163%, the transmission amplitude then increases by more than 98%.

Figure 3D shows the terahertz transmission power spectrum of the MXene/PVAc structure under different degrees of stretching. When the tensile strength reached 163%, the modulation of the transmission strength is approximately 281%.

To evaluate the modulation performance of the sample, the modulation factor (MF) is introduced and is defined as the change in the integrated terahertz power emission caused by the light excitation intensity:

![Figure 3](image1.png)

**Figure 3** | (A) Terahertz time-domain spectra of samples without MXene coating on a PVAc substrate under tensile and non-tensile conditions. (B) Terahertz time-domain spectra of samples coated with MXene on PVAc substrate under different tensile degrees. (C) Terahertz frequency-domain spectra of samples without MXene coating on PVAc substrate under tensile and non-tensile conditions. (D) Terahertz frequency-domain spectra of samples coated with MXene on PVAc substrate under different tensile degrees.

![Figure 4](image2.png)

**Figure 4** | Modulation factor (MF) of samples versus different tensile strengths.
MF = \int P_{\text{lux}}(\omega) d\omega - P_{\text{stretch}}(\omega) d\omega \\
\int P_{\text{lux}}(\omega) d\omega . \tag{1}

P_{\text{lux}}(\omega) d\omega \text{ and } P_{\text{stretch}}(\omega) d\omega \text{ are the powers of the terahertz signal in the relaxed state and the stretched state, respectively.}

Figure 4 shows the dependence of the MF on the tensile strength. When the tensile strength was 136%, MF increased by 1.96. When the tensile strength reaches 147%, MF increases to 2.12. When the tensile strength reaches 163%, MF increases to 2.81. The change range of MF also increases with the increase of tensile strength. Due to the limitation of material properties, the limit of tensile strength is about 170%. If the tensile degree exceeds this limit, the damage to the substrate cannot be recovered.

To explain the modulation mechanism in further depth, the variations in the conductivity of the samples with the tensile degree have been calculated. From these calculations, we can extract the transient frequency-dependent complex conductivity from the time-domain data of the transmitted THz pulses, denoted by \( E_{\text{stretch}}(\omega) \) and \( E_{\text{non-stretch}}(\omega) \). The transmission ratio \( T(\omega) \) of the Fourier transform of these two wave forms is related to the complex conductivity as follows [39]:

\[
T(\omega) = \frac{E_{\text{stretch}}(\omega)}{E_{\text{non-stretch}}(\omega)} = \frac{n + 1 + Z_0 d\sigma(\omega)}{n + 1 + Z_0 d\sigma(\omega)} \tag{2}
\]

Where \( Z_0 = 377 \Omega \) is the impedance of free space, \( n = 1.5 \) is the refractive index of the non-stretch PVAc substrate within the THz range, and \( d \) is the thickness of the MXene coating, which is estimated to be 150 μm from the results in Figure 1B. Figures 5A, B show the real part \( \sigma_r(\omega) \) and the imaginary part \( \sigma_i(\omega) \) of the conductivity of MXene coating under different tensile degrees, respectively. Because the THz signal is strongly attenuated by the modulators, the calculation results in the higher and lower frequency ranges are not reliable, and thus we have only presented data measured between 0.1 and 1.0 THz in Figures 5A, B. To make the TDS calculations more scientifically accurate, the electrical experiment was performed as a reference group, with results as shown in Figure 5C. The relationship between the resistance and the degree of stretching is derived from the I-V diagram using the relationship among the current, the voltage and the resistance. The black curve in Figure 5D shows the variation in the resistance of the sample with the degree of drawing, while the blue curve shows the variation in the conductivity of the sample with the degree of drawing. The figure shows that the sample's resistance increases as the tensile strength increases and the sample's conductivity decreases as the tensile strength increases. The increase of the tensile strength from 100 to 136% is also shown to have a significant effect on the modulation of the tensile strength; at 147 and 163%, the stretching degree has little effect on the modulation. This is consistent with the peak modulation and the MF of the terahertz radiation time-domain spectrum.

**CONCLUSION**

A flexible broadband terahertz modulator based on a strain-sensitive MXene/PVAc(latex) material is reported. It is found that the MXene can absorb nearly 80% of the THz waves through testing of sponge and latex substrate-based samples. The results obtained show that the transmission rate of the THz signal increases with increases in the...
degree of stretching. When the stretching degree reaches 136, 147 and 163%, the terahertz time-domain spectrum signals are modulated by 42, 67 and 98%, respectively. The maximum modulation of the terahertz projection power spectrum reaches 281%. Through an analysis based on THz TDS and comparison of the electrical properties of the samples, it is concluded that the conductivity of each sample decreases with increasing tensile strength. In addition, the trends for both properties are the same and the order of magnitude remains consistent. The results show that MXene is a type of terahertz modulator that can modulate the terahertz transmission signal intensity of a sample effectively by stretching that sample with a strong force to change the conductivity of the sample.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

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AUTHOR CONTRIBUTIONS

YL: Conceptualization, Methodology, Validation, Investigation, Writing-Original Draft; XL: Investigation; TY: Investigation; JL: Investigation; BL: Investigation; JS: Conceptualization, Funding acquisition; BZ: Supervision, Conceptualization, Writing-Reviewing and Editing, Funding acquisition; FW: Supervision, Conceptualization.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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