Research article

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Broadband and ultrafast all-optical switching based on transition metal carbide

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Abstract: Ultrafast all-optical switches have attracted considerable attention for breaking through the speed limitation of electric devices. However, ultrafast and high-efficiency all-optical switches based on two-dimensional (2D) materials can be achieved due to their strong nonlinear optical response and ultrafast carrier dynamic. For this reason, we propose the pump-probe method to achieve an ultrafast optical switcher with a response time of 192 fs and a switching energy of 800 nJ by using transition metal carbide (Nb_2C). The response time and switching energy are far smaller than that of the all-optical device based on the saturable absorption effect of 2D materials. It is believed that the Nb_2C -based all-optical switch provides a novel idea to achieve a high-performance all-optical device and has the potential for application in high-speed photonics processing.

Keywords: 2D materials; all-optical switch; MXene Nb_2C ; pump-probe spectroscopy.

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1 Introduction

With the coming of the 5-G era, traditional electronic devices face huge challenges to meet the growing demand in optical communication and computing from the generation, modulation, transfer, detection, and storage to process [1–4]. High-speed all-optical switching (<1 ps) is regarded as a promising method to replace electronics devices in signal processing and optical connection. The ultrafast modulation speed, ultra-low energy loss, and broadband modulation wavelength from visible to the mid-infrared range are still challenges [5–7]. According to their broadband absorption and ultrafast optical response, two-dimensional (2D) materials have made plentiful and breakthrough achievements in the field of optoelectronics [8–10]. So far, the all-optical modulators based on the saturable absorption [11, 12], optical Kerr effect [13–15] as well as a photothermal effect [16–19] of 2D materials and ultrafast terahertz photonic devices [20, 21] have been reported. In 2014, Li et al. achieve a response time of 2.2 ps (corresponding to a modulation rate of ~200 GHz) by taking advantage of saturable absorption characteristics of graphene, which brings the hope to resolve the difficulty in ultrafast information processing [12]. The response time of all-optical modulation based on the Kerr effect and the photothermal effect is concentrated on the sub-nanosecond and microsecond level, respectively, which cannot reach the demands of high-speed optical devices. So, it is necessary to explore new methods to improve the modulation speed [22]. All-optical switching based on the graphene-loaded metal-insulator-metal waveguide with switching energy of 35 fJ and a switching time of 260 fs is achieved by using the pump-probe method [22]. By using complementary metal-oxide-semiconductor technology, an on-chip graphene waveguide all-optical modulator with a saturation threshold of 1.38 pJ is obtained by pump-probe technology [23]. These works pave the way toward integrated high-performance photonic devices. Interestingly, perovskites and gallium phosphide as the nonlinear absorption element exhibit sub-20 fs and sub-30 fs

ultrafast optical response in the visible/near-infrared region by using the pump-probe method due to their Kerr effect and two-photon absorption [24, 25]. Therefore, exploring novel 2D materials is a significant topic to develop potential nanoscale devices for application in ultrafast and low-loss data processing and computing.

As an emerging 2D material, MXenes (transition metal carbides and/or nitrides) have attracted considerable attention due to their remarkable merits including ultrafast optical response, broadband optical absorption, effective energy conversion, and tunable optoelectrical properties [26–29]. The general formula of MXene is $M_{n+1}X_nT_x$ ($n = 1–4$) such as Ti_3C_2 , Ti_2C , Nb_2C , and V_2C , where M and T represent transition metal and surface terminations, respectively, X is carbon and/or nitrogen. Niobium-carbide (Nb_2C), the representative member of the MXene family after Ti_3C_2 , was fabricated in 2013 [30, 31]. Nb_2C MXene exhibits a stronger optical response and higher photo-thermal conversion efficiency than Ti_3C_2 MXene [32]. Ultrafast relaxation time (37 fs) and nonlinear optical properties (saturable absorption and reverse-saturable absorption) have been reported, and the carrier relaxation time of Nb_2C is far shorter than that of graphene, which has the potential for breakthrough improvement in broadband and ultrafast photonics and optoelectronic devices [33]. The first-principles method calculates the band structure of few-layer Nb_2C with a bandgap of ~ 1 eV, indicating Nb_2C has broadband optical absorption properties [33]. So far, Nb_2C has been widely studied as electrode materials for supercapacitors [34] and as photocatalysts for hydrogen evolution [35, 36], but there is an absence for nonlinear photonics application in optical switcher and modulator.

Herein, Nb_2C MXene nanosheets (NSs) were facilely fabricated by the acid etching method. We investigate the nonlinear optical properties and carrier dynamic process by the pump-probe method to achieve ultrafast and energy-efficient all-optical switch. The all-optical switch with a response time of 192 fs, an energy loss of 800 nJ, and transitivity modulation depth of 4% is achieved. It is anticipated that the all-optical switch based on 2D MXene paves the way toward ultrafast all-optical information processing.

2 Fabrication and characteristics of few-layer MXene Nb_2C

The detailed fabrication process of MXene is described in the experimental section. Figure 1(a) shows the scanning

electron microscope (SEM) image of the Nb_2AlC MAX precursor. Although layered structure can be observed in the edge of the Nb_2AlC powder, it is impossible to separate the MAX layers by traditional mechanical exfoliation owing to the strong M–A bonds. Fortunately, 2D MXenes can be fabricated by selective etching of the “A” element with hydrofluoric acid (HF). As shown in Figure 1(b), the slack accordion-like structure with multiple layers indicates the successful etching of the Al layer. Besides, the disappearance of the Al element in Nb_2C can be further confirmed by the X-ray photoelectron spectroscopy (XPS) results (Figure S1). Compared with the Nb_2AlC precursor, the peak at ~ 680 eV in Nb_2C can be assigned as an F element, which comes from the HF acid during the etching process. Therefore, the surface of as-fabricated Nb_2C is terminated with a hydrophilic group of $-F$, $-OH$, and $-O$, endowing it a good dispersion in water. To obtain few-layer Nb_2C NSs, tetrapropylammonium hydroxide aqueous solution was used to intercalate the as-synthesized multi-layer Nb_2C MXenes. As can be seen in Figure 1(c), the electron-transparent flakes indicate the ultrathin characteristic of as-exfoliated Nb_2C NSs. Besides, the large size distribution of Nb_2C NSs can be ascribed to the experimental procedure where the centrifugation between 3000 and 15,000 rpm was collected. Figure 1(d) demonstrates the high-resolution transmission electron microscopy image and a crystalline lattice with a hexagonal structure can be observed. The inset selected area electron diffraction pattern also confirms the hexagonal symmetry structure. To confirm the thickness of the Nb_2C NSs, atomic force microscopy (AFM) was carried out with the recorded results shown in Figure 1(e). Apparent 2D flakes can be observed in the AFM image while the inset height profiles indicate a uniform thickness of ~ 2.5 nm. Combining with the transmission electron microscope (TEM) and AFM results, the as-exfoliated Nb_2C NSs are proved to exhibit a typical 2D structure with an ultrathin feature. Figure 1(f) shows the UV–Vis spectrum of few-layer Nb_2C NSs in ethanol. The strong absorbance ranging from 200 to 1200 nm indicates that the few-layer Nb_2C NSs show a significant response to UV–Vis light, holding great potentials for novel optoelectronic devices. Moreover, the as-exfoliated few-layer Nb_2C NSs are quite stable in ethanol owing to the abundant hydrophilic terminations and the Tyndall effect remains after storage for more than one week.

3 Results and discussion

Figure 2 shows the experimental diagram of an all-optical switch. The ultrafast relaxation time of MXene Nb_2C is studied by the pump-probe technique based on ~ 100 fs laser.

Figure 1: (a) Scanning electron microscope (SEM) image of Nb_2AlC MAX powder. (b) SEM image of hydrofluoric acid-etched Nb_2C MXene. (c) Transmission electron microscope (TEM) image of few-layer Nb_2C nanosheets (NSs). (d) High-resolution TEM image of few-layer Nb_2C NSs. The inset image shows the corresponding selected area electron diffraction (SAED) pattern. (e) Atomic force microscopy image of few-layer Nb_2C NSs with marked height profiles. (f) UV-Vis-NIR spectra of the few-layer Nb_2C NSs. The inset is the Tyndall effect of the few-layer Nb_2C NSs in ethanol.

The pump light (420 nm) and probe light (500–1500 nm) are injected into the MXene Nb_2C solution. The delay time between two laser beams can be changed by the delay line. The supporting information provides more details about the pump-probe experimental setup.

Figure 3(a) shows the differential transitivity ($\Delta T/T$) results using pump light at the average power of 0.4 mW as a function of the wavelength of probe light and the pump-probe delay time. The dynamic relaxation process of the probe light is analyzed after interaction with both MXene and incident laser. When the delay time is larger than 0 fs, a modulation is up to 2% and decreases quickly to 0% within 1 ps, which results from the third-order nonlinear response of MXene due to the Kerr effect and two-photon absorption [24, 25]. The modulation depth increases toward the long

wavelength of the signal light. The modulation depth can be further improved by increasing the pump power and reducing the spot size of a laser beam. Figure 3(b) describes the differential transitivity spectra of the MXene at the delay time of $t = 174$ fs, which indicating broadband optical response in the visible wavelength. Figure 3(c) shows differential transitivity results by pumping the MXene with the wavelength of 420 nm at 0.4 mW, using the visible light (567 nm) as the probe light. A sign-flip and faint long-lived tails are observed in Figure 3(c). The sign-flip corresponds to the absorption bleaching. The bleaching induced by pump light reduces the absorption of the probe light. The electronic transitions cannot happen within the bandgap from the valence band to the conduction band. The differential transitivity as a function of delay time is fitted by a

Figure 2: Experimental diagram of an all-optical switch.

Figure 3: The experimental results of the pump-probe method.

(a) Differential transitivity spectra of MXene versus short wavelength of probe light and delay time. (b) Differential transitivity spectra of the MXene at the delay time of $t = 174$ fs. (c) The dynamic curves and fitted results of the MXene at 567 nm. (d) Full width at half maximum as a function of the wavelength of the probe light. (e) The dynamic curves under different pump power. (f) The pump power dependence of differential transitivity at 622 nm with linear fitting.

biexponential function $\Delta T/T = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where t represents the delay time between the pump light and probe light, A is the amplitude, and τ is the time constant corresponding to the lifetime of the carrier relaxation process. The fast and slow time constants can be regarded as the electron-phonon interaction and phonon-phonon interaction. The electron relaxation processes (energy dissipation processes) occur in two procedures. First, the photo-excited electrons interact with other electrons near the Fermi level and reach electron thermalization. The photon-excited electrons rapidly form hot electrons via electron-electron collision and the resultant hot electrons have the same electronic temperature. Then, the high-excited state electrons mainly interact with optical phonons. The excess energy in optical phonon can dissipation and the electrons lose their excess momentum, relaxing to the minimum point of excited states. The temperature between electron and optical phonon reaches accordance, resulting in thermal equilibrium. Fitting the time constants, the MXene possesses ultrafast relaxation time with τ_1 of 37.4 fs and τ_2 of 710 fs at 567 nm, establishing a good basis to achieve high-performance optoelectronic

devices. The MXene possesses ultrafast relaxation time with τ_1 of 37.4 fs and τ_2 of 710 fs at 567 nm, establishing a good basis to achieve high-performance optoelectronic devices. The relaxation time can be further shortened by the defect engineering method and the size of the flake of MXene. The carrier dynamic of MXene is much shorter than those of other 2D materials such as graphene, WS_2 , and black phosphorus [37–41]. Besides, the dynamic curve presents a full width at half maximum (FWHM) of 192 fs with switching energy of 800 nJ, which can reach the modulation speed of THz. Resonators with a high Q factor achieve the comparable performance of optical switching, but the response time is limited by the cavity lifetime to the picosecond/nanosecond level [42, 43]. MXene-based all-optical modulation exhibits a faster response time. In Figure 3(d), the FWHM versus the wavelength of probe light ranged from 550 to 720 nm are described. The FWHM is concentrated on the range from 200 to 250 fs. The ultrafast carrier dynamic of MXene opens a door to achieve breakthrough progress in ultrafast photonics and high-speed optical switcher. With the increase of the pump power, the differential transitivity of the dynamic curve increases at

Figure 4: (a) Differential transitivity spectra of MXene versus long wavelength of probe light and delay time at the near-infrared region. (b) Differential transitivity spectra of the MXene at the delay time of $t = 120$ fs. (c) The dynamic curves and fitted results of the MXene at 902 nm.

567 nm, as shown in Figure 3(e). Figure 3(f), the pump power dependence of differential transitivity at 567 nm with a linear fitting exhibits 3.85% of modulation depth, indicating nondegenerate optical Kerr effect and two-photon absorption state without saturation behavior.

Moreover, Figure 4(a) shows the differential transitivity results using pump light at the average power of 0.4 mW as a function of the wavelength of probe light from 900 to 1320 nm and the pump-probe delay time. When the delay time is larger than 0 fs, a modulation is up to 2.6% and decreases quickly to 0% within 1 ps. Figure 4(b) describes the differential transitivity spectra of the MXene at the delay time of $t = 120$ fs, which indicating broadband optical response in the infrared region. Figure 4(c) shows differential transitivity results by pumping the MXene with the wavelength of 420 nm at 0.4 mW, using the visible light (902 nm) as the probe light. A sign-flip and faint long-lived tails are observed in Figure 4(c). The sign-flip corresponds to the absorption bleaching. The bleaching induced by pump light reduces the absorption of the probe light. The MXene possesses ultrafast relaxation time with τ_1 of 153 fs and τ_2 of 2.37 ps at 902 nm, establishing a good basis to achieve high-performance optoelectronic devices. Besides, the dynamic curve presents an FWHM of 239 fs, indicating that the all-optical switch with a $\sim$ fs response time and a broadband modulation is proposed. The pump-probe method takes full advantage of the ultrafast carrier dynamic of MXene to achieve high-performance all-optical devices. It is believed that the MXene-based all-optical switch opens a door to practical applications of 2D materials in all-optical signal processing.

4 Conclusion

In conclusion, MXene NSs are prepared by the acid etching method. By SEM, TEM, AFM, and spectrometer instruments, MXene Nb_2C possesses a few-layered structure and broadband optical absorption. An ultrafast and broadband all-optical switching with a response time of 192 fs and switching energy of 800 nJ is demonstrated, illustrating pump-probe technology is an effective way to improve modulation speed by using the ultrafast carrier dynamic in 2D materials. It is believed that exploring the ultrafast response of 2D materials and developing pump-probe technology are promising research directions to achieve high-performance photonics devices.

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