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Ultrafast dynamics of photoexcitations in 2D $Ti_3C_2T_z$, $Mo_2Ti_2C_3T_z$, and Nb_2CT_z MXenes

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ABSTRACT

MXenes are a new class of intrinsically metallic 2D materials. Their wide range of optoelectronic properties they demonstrate as a function of their chemical composition suggest applications in electronic and photonic devices. In this work we present a comprehensive study of the optical properties of three members of the MXene family, $Ti_3C_2T_z$, $Mo_2Ti_2C_3T_z$, and Nb_2CT_z, using ultrafast transient optical absorption and THz spectroscopy. We find that those properties result from a complicated interaction between free carriers, interband transitions and localized surface plasmon resonances. Elucidating the nature of photoexcitation and dynamics of carriers in these emergent materials will lay the foundation for their potential for optoelectronic applications.

Keywords: MXene, 2D materials, Plasmon, Transient Absorption Spectroscopy, THz spectroscopy

1. INTRODUCTION

MXenes are an emergent 2D material class of transition metal carbides, nitrides and carbonitrides with a general formula $M_{n+1}X_nT_z$, where M is a metal, X = C or N, and n = 1–3; T_z stands for the surface terminations –OH, –O, and/or –F.[1,2] Electronic properties of MXenes are determined by specific chemistries, surface terminations, as well as by water molecules and cations that are introduced during fabrication and occupy the van der Waals gaps between individual MXene nanosheets. MXenes demonstrate many attractive properties, record conductivity and capacitances,[3] high optical nonlinearities, high laser damage thresholds, and pronounced plasmonic effects. [4,5]

A variety of electronic and photonic applications of MXenes such as electromagnetic interference (EMI) shielding[6], energy storage, and plasmonic devices have been proposed, but the electronic and optical properties of this family have not yet been fully understood. It has been shown that optical properties can be tailored by changes in structure and morphology [7, 8, 9]. Recently, a study of optical excitation of different MXene chemistries by Maleski et al, showed that optical extinction peaks for Ti_2C and Ti_3C_2 at 2.25eV and 1.6eV respectively corresponds to localized surface plasmon resonances in the visible to near IR range.[7] Such property is already being used in surface-enhanced Raman spectroscopy[10] and optical fibers in telecommunications[11]. However, the plasmonic nature of the observed visible-near IR resonances is still under debate.

In this work, we investigate the photoexcitation-induced changes in optical properties of 2D MXenes with different chemical compositions. We study drop coated thin films of 2D Ti_3C_2, $Mo_2Ti_2C_3$, and Nb_2C using two complementary spectroscopy techniques: ultrafast transient optical absorption (TA) which provides information about the photoexcited states and their lifetimes as well as changes in absorption in the optical range and the timescales over which absorption returns to the pre-excitation spectrum, and THz spectroscopy that give us information about the free carriers and the transient changes in photoconductivity.

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2. RESULTS AND DISCUSSION

Figures 1 (a), 1(b) and 1(c) shows the static absorption spectra of all three compounds studied. Broad absorption peaks were found at 750nm for Ti_3C_2 and a peak at 520nm for $Mo_2Ti_2C_3$.[12] Previously, this peak in Ti_3C_2 has been ascribed to a localized surface plasmon resonance (LSPR).[7,13] For Nb_2C, previous reports showed an absorption peak centered at 950nm[7], while in our film, a very weak but discernable absorption feature appears, at 730nm.[12]

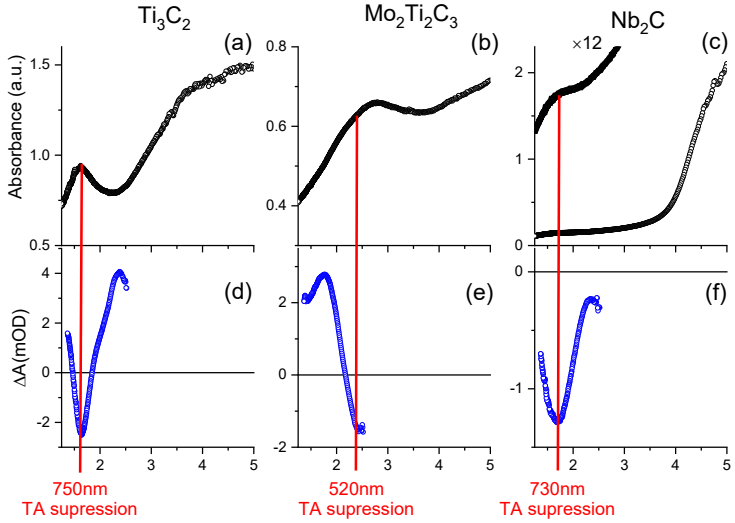

Figure 1. (a), (b), (c) Static absorption and (d) ,(e) ,(f) Transient absorption with 400nm pump of 2D Ti_3C_2, $Mo_2Ti_2C_3$ and Nb_2C thin films

The films were excited by either 400nm or 800nm pump, thus allowing excitation either below or above the static absorption peak. TA results show a suppression of absorption that is centered at exactly the energies of the peaks observed in the static absorption spectra of every MXene, as indicated in Figure 1(d), 1(e) and 1(f). This behavior was found to be independent of the excitation energy or fluence.

The photo-induced suppression of absorption at the plasmon resonance is well known in bulk and nanoscale metals. When the free electron distribution of a metal is optically excited, a non-equilibrium hot carrier distribution is created over sub-ps time scales as a result of electron-electron interactions.[14] The hot carrier distribution relaxes by electron-phonon interactions, it transfers its energy to the crystal lattice over times scales ranging from sub-ps to several ps. Increased temperature results in broadening of the plasmon resonance, appearing as suppression of absorption at its peak. Eventually, lattice cools by transferring thermal energy to the surroundings, via thermal diffusion and/or radiation.[15,16,17] Lattice cooling can therefore be observed as the recovery of the suppression of absorption in TA.

In our films, suppression of absorption can be observed in Figure 2(a), 2(c) and 2(e) at different delay times. These measurements suggest that Vis-near IR absorption features can be attributed to a plasmon, which, in turn, confirms the existence of plasmonic features, not only in Ti_3C_2, as was expected, but in $Mo_2Ti_2C_3$ and Nb_2C as well. This renders possible the supposition of more MXenes chemistries having plasmonic features as well.

As can be seen in figure 2(a), the recovery time scales of the suppression of absorption were found to be very long. In Ti_3C_2, full thermal relaxation is found to be longer than our detection limit, at 3ns. In $Mo_2Ti_2C_3$, Figure 2(c), was also measured to be ~3ns, whereas Nb_2C , Figure 2(e), it recovers on ~ 100 ps time scales.[12] Thermal transport typically has two major contributions, characterized by the carrier and lattice thermal conductivity. A recent investigation suggested that electron-phonon scattering in Nb_2C is at unusually strong, and comparable to the phonon-phonon scattering, the predominant mechanism limiting thermal transport in 2D materials.[18] If this holds true for other MXenes as well, scattering of phonons by the free carriers may turn out to be the reason for the slow thermal relaxation revealed by the TA spectroscopy.

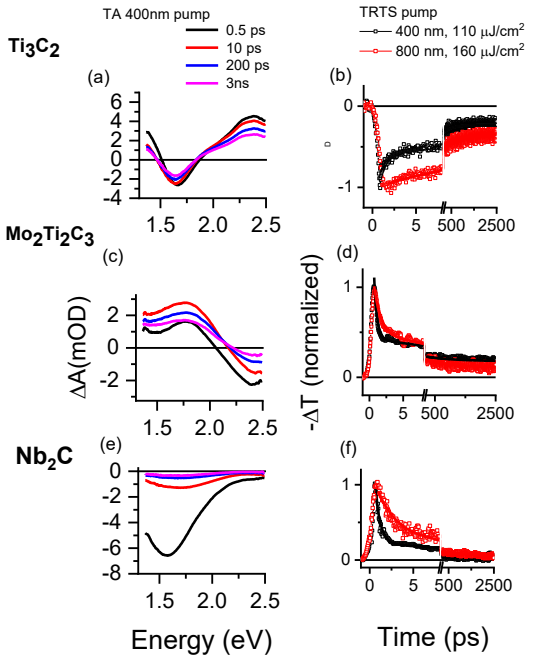

Figure 2. (a) ,(c), (d) Transient absorption at different delay times, (b), (d) ,(e) Time-resolved THz spectroscopy of 2D Ti_3C_2, $Mo_2Ti_2C_3$ and Nb_2C thin films

To investigate the relation between free carrier density and slow thermal conductivity, we carry out THz spectroscopy measurements on the same films. Intrinsic conductivity is directly proportional to carrier density and can be deduced from the THz TDS spectroscopy. We find that Ti_3C_2 presents with the highest conductivity ≈3500 $(\Omega\ cm)^{-1}$, followed by $Mo_2Ti_2C_3$ with lower conductivity ≈ 160 $(\Omega\ cm)^{-1}$, and then Nb_2C where the conductivity was below the detection range.[12]

It has been reported for Ti_3C_2 films experimental room temperature thermal conductivity of 2.84 W m^{-1} K^{-1}, orders of magnitude lower than for conventional metals. [19,20] Additionally, the Wiedemann-Franz law analysis relating experimental electrical and thermal conductivity values for a Ti_3C_2 film shows that electronic contribution to the measured thermal conductivity is only ~ 2-3%.[21]

From optical pump THz probe spectroscopy, we can obtain the changes in carrier density and conductivity, under photoexcitation at 400nm and 800nm. Figure 2(b), 2(d) and 2(f) shows that relaxation times depend on excitation and fluence, probably due increasing of inter-band excitation of carriers. We observe in Figure 2(b) the slowest lattice cooling ~3ns corresponds to the MXene with higher free carrier density, Ti_3C_2, for $Mo_2Ti_2C_3$ the lattice cooling is also slow, Figure 2(d), and the fastest recovery ~ 100 ps in Nb_2C, Figure 2(f). THz spectroscopy results shows that free carries in the studied MXene films presumably limit thermal diffusion where in Nb_2C the free carriers are almost exclusively optically injected.

TA and THz spectroscopy results obtained in this study provides evidence to the unprecedently low lattice thermal conductivity in MXenes, strong electron-phonon scattering responsible for unusually low thermal conductivity agrees with the highly efficient photothermal conversion efficiency in MXenes.

3. SUMMARY

In all three MXenes, photoexcitation is found to result in suppression of absorption of the plasmon resonances which recovers fastest in the MXenes with lower free carrier density (intrinsic conductivity). The presence of plasmonic features in Ti_3C_2 has been verified and it has been shown, that $Mo_2Ti_2C_3$ and Nb_2C possess plasmonic features as well. TA and THz results confirmed low lattice thermal conductivity and slow heat dissipation due to strong carrier-phonon scattering in MXenes.

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