

PROCEEDINGS OF SPIE

SPIDigitalLibrary.org/conference-proceedings-of-spie

Probing photoexcited free carrier dynamics of two-dimensional MXene, Nb₂C, using ultrafast terahertz spectroscopy

Andrew Fitzgerald, Erika Colin-Ulloa, Javery Mann, Kiana Montezari, Michel Barsoum, et al.

Andrew M. Fitzgerald, Erika Colin-Ulloa, Javery A. Mann, Kiana Montezari, Michel W. Barsoum, Lyubov V. Titova, "Probing photoexcited free carrier dynamics of two-dimensional MXene, Nb₂C, using ultrafast terahertz spectroscopy," Proc. SPIE 12419, Ultrafast Phenomena and Nanophotonics XXVII, 124190K (15 March 2023); doi: 10.1117/12.2650359

SPIE.

Event: SPIE OPTO, 2023, San Francisco, California, United States

Probing Photoexcited Free Carrier Dynamics of Two-Dimensional MXene, Nb₂C, Using Ultrafast Terahertz Spectroscopy

Andrew M. Fitzgerald¹, Erika Colin-Ulloa¹, Javery A. Mann¹, Kiana Montezari², Michel W. Barsoum², Lyubov V. Titova¹

¹Worcester Polytechnic Institute, Worcester, MA; ²Drexel University, Philadelphia, PA

ABSTRACT

Discovered in 2013, 2D niobium carbide (Nb₂C), a member of the MXene family, has been shown to have many extraordinary properties, such as high photothermal conversion efficiency, strong electron-phonon interactions, strong optical absorption in the near-infrared, and even saturable optical absorption. These unique properties of Nb₂C render this MXene potentially useful for a variety of applications, including photonic and optoelectronic devices and even photothermal cancer therapy. Here, we employ both terahertz time-domain spectroscopy (TDS) and time-resolved terahertz spectroscopy (TRTS) to investigate intrinsic and photoinduced conductivity and dynamics of optically injected charge carriers with 1.55 eV excitations in order to understand the photoinduced processes taking place in Nb₂C. We find that the photoinduced conductivity in this MXene shows an initial rapid decay over a picosecond time scale, followed by a much longer-lived component that lasts for nanoseconds. We also observe that the long-range conductivity is strongly limited by the nanoflake boundaries.

Keywords: Terahertz spectroscopy, MXenes, Nb₂C, charge carrier transport

1. INTRODUCTION

MXenes are an emerging class of two-dimensional materials comprised of transition metal carbides, nitrides, and carbonitrides that were first discovered in 2011. These materials share the same general chemical formula $M_{n+1}X_nT_x$ in which M is a transition metal, X is carbon or nitrogen, n takes a value from 1 – 4, and T_x denotes the surface terminations of the material (e.g. –OH, –O, and/or –F).^[1] Named for the way they are synthesized, MXenes are derived from their parent MAX-phases by selectively etching away the A-element (usually Al). Some of these newly discovered materials have exhibited outstanding properties, such as record high volumetric capacitances, high conductivities, and nonlinear optical properties, rendering them potentially useful for applications in energy storage, electromagnetic interference shielding, photonic and optoelectronic devices, and much more.^[2] Their extensive and diverse list of outstanding properties and applications highlights the importance of understanding the charge carrier transport mechanisms of MXenes and how they differ between different MXene compounds.

This work seeks to gain a better understanding of the charge carrier transport mechanism of Nb₂C, a MXene discovered in 2013^[3] that has since exhibited many extraordinary properties, including a high photothermal conversion efficiency^[4], nonlinear optical properties^[5], a low charge carrier density^[2], and a negligibly low conductivity^[2] (unlike similar MXenes, such as Ti₃C₂, Ti₂C, or V₂C). Its unique properties allow this MXene to find itself useful in a variety of applications, such as photothermal cancer therapy^[4], photonic devices^[3], optoelectronic devices^[3], and more. In our recent study, we have demonstrated that Nb₂C exhibits a weak surface plasmon resonance centered around 750 nm^[9], despite negligibly low intrinsic free carrier density. Here, we explore the properties of photoexcited carriers in this material using time-resolved THz spectroscopy.

2. METHODS

2.1 Synthesis

Samples of Nb₂C were synthesized by selectively etching away Al from its parent MAX phase, Nb₂AlC, before delamination using TMAOH as an intercalant. Nb₂C was then drop-cast onto IR-grade quartz to produce ~0.5 – 1 μm thick films to be used for optical measurements made by terahertz (THz) spectroscopy.

2.2 Terahertz spectroscopy

THz spectroscopy is an all-optical spectroscopic technique that is used to probe free carrier absorption and other low-energy processes in a material. Utilizing THz frequency pulses of light that have durations on the order of picoseconds and photon energies in the range of 1 – 10 meV (0.25 – 2.1 THz bandwidths), it is a contactless tool that can be used to access the complex intrinsic conductivity and photoconductivity of a material. In this work, two different methods of THz spectroscopy are employed to investigate the intrinsic and photoinduced conductivity and dynamics of optically injected charge carriers with 1.55 eV optical excitations in order to understand the photoinduced processes taking place in Nb₂C.

The first method is known as THz time-domain spectroscopy (TDS), and it is used to extract intrinsic properties from a material, such as complex index of refraction, absorption coefficient, and complex conductivity. The second method is known as time-resolved THz spectroscopy (TRTS), and it is used to study the effects that photoexcitations have on a material's intrinsic properties and its charge carrier transport mechanism.

3. RESULTS AND DISCUSSION

3.1 TDS

TDS was used to extract the complex conductivity of Nb₂C (and Ti₃C₂ for comparison, the first MXene to be discovered^[1]). Figure 1 shows a plot of the real conductivity for both Nb₂C and Ti₃C₂ as a function of the frequencies encompassed in the bandwidth of the THz pulses used in these measurements. In concurrence with the literature, it is found that Nb₂C has a negligibly low intrinsic conductivity, unlike the highly conductive Ti₃C₂. We note here that our recent study showed a very weak, broad plasmon resonance feature in the near-IR, indicating that a small free carrier density is indeed present in Nb₂C films. The resulting conductivity is, however, below the detection limit in our TDS setup. Density functional modeling of Nb₂C also suggests that it is indeed metallic when terminated with -OH and -O groups rather than with nitrogen.^[10] We posit that it is metallic with an exceedingly low density of states at the Fermi level.

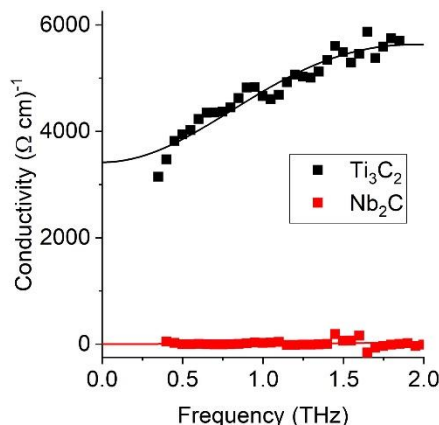


Figure 1: The real part of intrinsic conductivity of both Nb₂C and Ti₃C₂ extracted from TDS measurements.

3.2 TRTS

TRTS measurements were performed on Nb₂C using 1.55 eV excitations with 2 mJ/cm² fluences. Figure 2 shows a plot of the change in transmission of THz pulses through Nb₂C as the sample is photoexcited. From the plot, it can be seen that there is a rapid decrease in THz transmission (corresponding to a rapid onset of enhanced photoconductivity) due to the photoexcitation that is followed by a long (~3 ns) relaxation time. This rapid onset of enhanced photoconductivity is similar to what is seen in Mo₂Ti₂C₃^[6], Mo₂TiC₂^[6], and Nb₄C₃^[7] but opposite to the rapid decrease in photoconductivity that is seen in Ti₃C₂. This optically induced onset of conductivity suggests that it is a result of inter-band injection of charge carriers.

The relaxation behavior after photoexcitation of Nb₂C consists of three components and was fit to a three-exponential function. The fastest component lasts for ~1.7 ps and is attributed to carrier-carrier and carrier-phonon scattering. The next fastest component lasts for ~26 ps and is attributed to carrier trapping at defects in the material.^[5] The longest component persists for ~3 ns in which a small fraction of the charge carriers in the material are surviving long after photoexcitation.

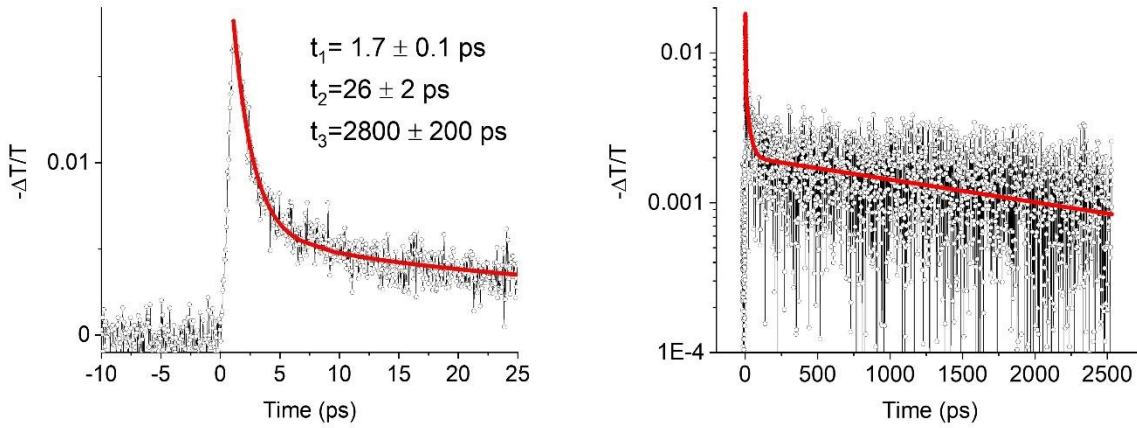


Figure 2: The change in THz transmission through Nb₂C due to 1.55 eV, 2 mJ/cm² fluence photoexcitation over time with the left window showing up until 25 ps and the right window zoomed out to show up until 2.5 ns.

3.3 TRTS photoconductivity spectra

Using TRTS, photoconductivity spectra can also be obtained for Nb₂C. Figure 3 shows the photoconductivity spectra at 1, 2, 3, 5, and 10 ps after initial 1.55 eV photoexcitation of the sample fit to the Drude-Smith model^[8] in which complex, frequency-resolved conductivity is given as:

$$\tilde{\sigma}(\omega) = \frac{Ne^2\tau_{DS}/m^*}{1-i\omega\tau_{DS}} \left(1 + \frac{c}{1-i\omega\tau_{DS}}\right). \quad (1)$$

In the Drude-Smith model, N is the charge carrier density, m^* is the charge carrier effective mass, τ_{DS} is scattering time, and c is the localization parameter. The localization parameter takes a value between -1 and 0. When $c = -1$, conductivity is suppressed, and charge carriers are localized over short distances. When $c = 0$, charge carriers are moving throughout a sample completely unimpeded.^[6]

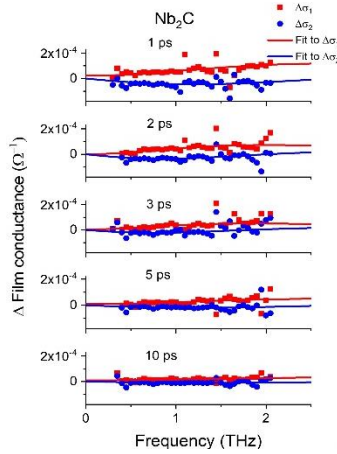


Figure 3: Photoconductivity spectra of Nb₂C at multiple times intervals after 1.55eV photoexcitation

In figure 4, both the localization parameter and scattering time for each of the five spectra are plotted as a function of time. Both parameters remain constant over time with the localization parameter having a value of ~ -0.94 and the scattering time being ~ 65 fs. This scattering time is comparable to the scattering time measured for a similar MXene, Nb₄C₃, whose scattering time was ~ 50 fs; however, the localization parameters of these two MXenes are very different with Nb₄C₃ taking a value of ~ -0.7 .^[7] Because the localization parameter of Nb₂C is much closer to -1, it is found that the charge carriers in Nb₂C are much more localized than in Nb₄C₃, possibly as a result of a smaller thickness of individual flakes.

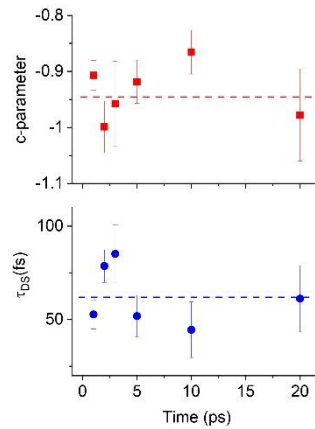


Figure 4: Photoconductivity spectra parameters from the Drude-Smith model for complex conductivity

The effective mass of free carriers in -O and -OH terminated Nb₂C has not yet been reported, so we cannot estimate carrier mobility. However, from the c-parameter, we find that the short-range, intra-flake charge carrier mobility ($\mu_{(SR)}$) is ~ 17 times higher than the long-range, inter-flake carrier mobility ($\mu_{(LR)}$):

$$\frac{\mu_{(SR)}}{\mu_{(LR)}} = \frac{1}{1+c} = 16.67. \quad (2)$$

Free carriers are strongly localized within Nb₂C nanoflakes, and there is little transport between individual flakes. Future work will focus on improving the photoexcited carrier lifetime by post-processing and improving inter-flake connectivity.

ACKNOWLEDGEMENTS

Approved for public release by DEVCOM Soldier Center: PAO# PR2023_59160. This work was supported in part by NSF DMR 2018326 and 1740795 awards and by the US Army DEVCOM Soldier Center AA1 basic research program. AMF was supported by NSF NRT CEDAR Fellowship, Award Number 2021871.

REFERENCES

- [1] Naguib, M., Kurtoglu, M., Presser, V., Lu, J., Niu, J., Heon, M., Hultman, L., Gogotsi, Y., and Barsoum, M.W., “Two-dimensional nanocrystals produced by exfoliation of Ti_3AlC_2 ,” *Adv. Mater.*, 23, 4248-4253 (2011).
- [2] Maleski, K., Shuck C.E., Fafarman A.T., and Gogotsi, Y., “The broad chromatic range of two-dimensional transition metal carbides,” *Adv. Optical Mater.*, 9, 2001563 (2021).
- [3] Naguib, M., Hamlin, J., Lu, J., Cook, K., Hultman, L., Gogotsi, Y., and Barsoum, M.W., “New two-dimensional niobium and vanadium carbides as promising materials for Li-ion batteries,” *J. Am. Chem. Soc.*, 135, 43, 15966–15969 (2013).
- [4] Lin, H., Gao, S., Dai, C., Chen, Y., and Shi, J., “A two-dimensional biodegradable niobium carbide (MXene) for photothermal tumor eradication in NIR-I and NIR-II biowindows,” *J. Am. Chem. Soc.*, 139, 16235-16247 (2017).
- [5] Gao, L., Chen, H., Zhang, F., Mei, S., et. al., “Ultrafast relaxation dynamics and nonlinear response of few-layer niobium carbide MXene,” *Small Methods*, 4, 2000250 (2020).
- [6] Li, G., Natu, V., Shi, T., Barsoum, M.W., and Titova L.V., “Two-dimensional MXenes $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_z$ and $\text{Mo}_2\text{TiC}_2\text{T}_z$: microscopic conductivity and dynamics of photoexcited carriers,” *ACS Appl. Energy Mater.*, 3, 1530-1539 (2020).
- [7] Zheng, W., Sun, B., Li, D., Manoj Gali, S., et. al., “Band transport by large Fröhlich polarons in MXenes,” *Nat. Phys.*, 18, 544–550 (2022).
- [8] Smith, N.V., “Classical generalization of the Drude formula for the optical conductivity,” *Phys. Rev. B*, 64, 155106 (2001).
- [9] Colin-Ulloa, E., Fitzgerald, A., Montazeri, K., Mann, J., Natu, V., Ngo, K., Uzarski, J., Barsoum, M. W., Titova, L. V., “Ultrafast Spectroscopy of Plasmons and Free Carriers in 2D MXenes,” *Adv. Mater.*, 2208659 (2022).
- [10] Li, G., Li, N., Peng, S., He, B., Wang, J., Du, Y., Zhang, W., Han, K., Dang, F., “Highly Efficient Nb₂C MXene Cathode Catalyst with Uniform O-Terminated Surface for Lithium–Oxygen Batteries,” *Adv. Energy Mater.*, 11, 2002721 (2021).