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Two-dimensional Niobium Carbide MXene, Nb_2CT_x: intrinsic and photoexcited carrier dynamics

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***Abstract*— Garnering attention for high conductivity, nonlinear optical properties, and more, MXenes are water-processable 2D materials that are considered candidates for applications in electromagnetic interference shielding, optoelectronic and photonic devices among others. Herein we investigate the intrinsic and photoexcited conductivity in Nb_2CT_x, a MXene with reported high photothermal conversion efficiency. DFT calculations show that hydroxyl and/or fluorine-terminated Nb_2CT_x (T_x = OH or F) is metallic, in agreement with THz spectroscopy, which reveals the presence of free charge carriers that are highly localized over mesoscopic length scales. Photoexcitation of Nb_2CT_x, known to result in rapid heating of the crystal lattice, is found to produce additional free carriers and a transient enhancement of photoconductivity. Most photoexcited carriers decay over the sub-picosecond time scales while a small fraction remain for much longer, sub-nanoseconds, times.**

I. INTRODUCTION

MXENES, a family of 2D transition metal carbides, nitrides, and carbonitrides, were initially identified in 2011. These materials share the general chemical formula $M_{n+1}X_nT_x$, where M denotes a transition metal, X stands for carbon or nitrogen, n takes on a value from 1 – 4, and T_x denotes the surface terminations, such as –OH, –O, or –F, that result from the MXene synthesis process, which involves selective etching of the A-element (typically Al) from their parent MAX-phases[1]. Several of these materials have exhibited remarkable properties, including record volumetric capacitances, high conductivity, and nonlinear optical properties, making them potential candidates for energy storage, electromagnetic interference shielding, optoelectronic and photonic devices, and many other applications.[2] The diverse array of exceptional properties and applications of MXenes underscores the importance of understanding their charge carrier transport mechanisms and how they differ between different MXene materials.

Since 2013[3], 2D niobium carbide MXene, Nb_2CT_x, has been attracting attention for its high photothermal conversion efficiency[4], nonlinear optical properties[5], as well as for a low charge carrier density and conductivity[2], unlike that of other MXenes, such as $Ti_3C_2T_x$, Ti_2CT_x, or V_2CT_x, where the carrier density is higher. These features make Nb_2CT_x a promising material for a wide range of applications, such as the development of photonic and optoelectronic devices and even for photothermal cancer treatments. In our recent work, we have demonstrated that Nb_2CT_x exhibits a surface plasmon resonance centered around 750 nm[6], despite having a low intrinsic free carrier density. Here, we explore the properties of intrinsic and photoexcited carriers in this material using time-domain and time-resolved THz spectroscopy and density functional theory (DFT) calculations with the aim of further understanding the charge carrier transport mechanism in Nb_2CT_x.

II. RESULTS AND DISCUSSION

Previous studies have reported a negligibly small conductivity in Nb_2CT_x[2], raising a possibility that Nb-based MXenes are semiconducting rather than metallic in nature; however, observed plasmonic properties indicate the presence of free charge carriers[6]. Our DFT calculations reveal that C, F, O, and H atoms have negligible contributions to the electronic structure near the Fermi level, and the d-orbitals of Nb atoms dominate, resulting in a metallic nature for bare Nb_2C and all Nb_2CT_x structures with F and/or OH terminations. The only termination that yields a narrow-bandgap semiconductor with a bandgap of 0.71 eV is nitrogen (Nb_2CN_2), as the p-orbitals of nitrogen bond with the d-orbitals of niobium, resulting in a gap around the Fermi level, in qualitative agreement with previous reports [7].

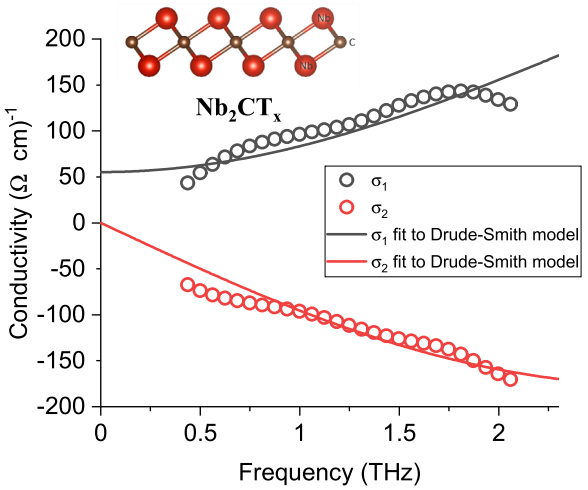

Fig. 1. Real (black) and imaginary (red) intrinsic conductivity of Nb_2CT_x films with fits to the Drude-Smith model. Inset: schematic of Nb_2CT_x monolayer structure with no terminations. Here, red represent Nb and brown is C.

To further investigate this experimentally, Nb_2CT_x was synthesized by selectively etching away Al from its parent MAX phase, Nb_2AlC, before delamination using TMAOH as an intercalant. Nb_2CT_x colloids were then spray-cast onto IR-grade quartz to produce ~0.5 – 1 μm thick films that were used for THz measurements. This results in multilayer films

consisting of many individual nanoflakes with sub-µm lateral dimensions. In such films, the transport properties result from a complicated interplay of intra-flake carrier motion, and long-range, inter-flake hopping transport.[8,9]

With photon energies of 1 – 10 meV, THz pulses are used to probe a material's free carrier absorption and enable us to access the complex intrinsic conductivity and photoconductivity. THz time-domain spectroscopy (THz-TDS) measurements were used to extract the complex conductivity of Nb_2CT_x. Figure 1 shows a plot of the real and imaginary parts of the intrinsic THz conductivity. We found that Nb_2CT_x has a low but finite intrinsic conductivity, ~ 2 orders of magnitude lower than other MXenes like $Ti_3C_2T_x$.

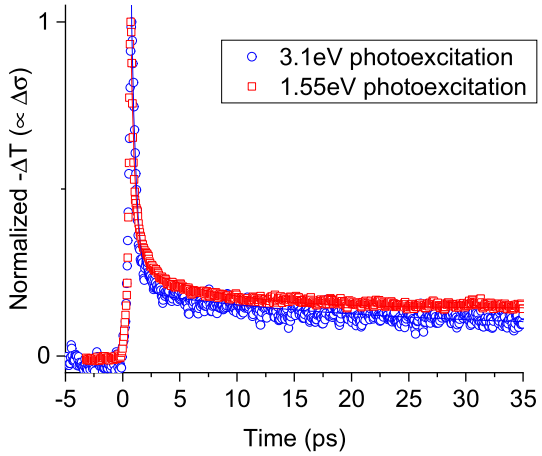

Fig. 2. Measured change in THz transmission through Nb_2CT_x normalized and plotted vs. time for both 1.55eV (red) and 3.1eV (blue) photoexcitations.

Fitting the experimental data to the Drude-Smith model for complex conductivity [8,10], given by

$$\tilde{\sigma}(\omega) = \frac{\sigma_0}{1-i\omega\tau_{DS}}\left(1 + \frac{c}{1-i\omega\tau_{DS}}\right), \quad (1)$$

we find that the localization parameter, c = - 0.9±0.1, and the scattering time τ_{DS} = 22±2 fs. In the Drude-Smith model, the localization parameter takes on a value between 0 and -1. For c = 0, charge carriers move throughout a sample entirely unimpeded, and for c = -1, the movement of charge carriers is suppressed or localized. Here the c parameter is close to -1, suggesting that charge carriers are highly localized over the distances comparable to the mean free path, either due to defects or edges of individual nanoflakes. As a result, static conductivity can be extrapolated as $\sigma_{DC} = \sigma_0(1 + c) = 60\pm10$ $(\Omega\ \text{cm})^{-1}$.

In time-resolved THz spectroscopy measurements, we introduce a photoexcitation (either at 1.55eV or 3.1eV) and measure the transient THz photoconductivity of Nb_2CT_x. Figure 2 shows the normalized change in THz transmission (which is proportional to the photoconductivity) when photoexcited with 1.55eV and 3.1eV. We find that photoexcitation of the sample (for both photoexcitation energies) results in a rapid onset of enhanced photoconductivity as interband excitations inject a new population of free carriers (electrons and holes). Photoconductivity then exhibits a significant decay within the first few picoseconds, ps, with a fast decay component of ~ 0.4 ps for both excitations, followed by a much slower decay on the order of hundreds of ps.

This is very similar to the behavior of other MXenes including $Mo_2Ti_2C_3T_x$[8], $Mo_2TiC_2T_x$[8], and $Nb_4C_3T_x$[9] but opposite to the rapid decrease in photoconductivity that is seen in highly conductive $Ti_3C_2T_x$. Rapid relaxation of the majority of free photoexcited carriers in Nb_2CT_x and previously reported high photothermal conversion efficiency suggests that the majority of the injected carriers, that recombine on sub-ps time scale, transfer their excess energy to the lattice, resulting in its fast and sustained heating.

In summary, our DFT calculations and THz spectroscopy experiments suggest that Nb_2CT_x is a metal with a small but finite intrinsic carrier density. The free carriers are strongly localized within individual MXene flakes, and photoexcitation across the visible-near infrared range injects additional free carriers that rapidly decay, transferring their excess energy to the lattice. These properties render this new 2D MXene promising not only for photothermal applications but also for ultrafast photonic devices.

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