Dynamics of Photoexcitations in $Ti_3C_2T_z$, $Mo_2Ti_2C_3T_z$, and Nb_2CT_z 2D MXenes

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***Abstract*—MXenes are intrinsically metallic 2D materials. We apply optical pump-THz probe and optical pump-optical probe spectroscopy to unravel the relationships between MXene chemistry, structure, and nature and dynamics of photoexcitations in three MXenes with different chemistries, $Ti_3C_2T_z$, $Mo_2Ti_2C_3$, and Nb_2CT_z.**

I. Introduction

MXenes are an emergent 2D material class. MXenes are 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 denotes surface terminations such as –OH, –O, and/or –F.[1,2] Unlike most other 2D materials, MXenes are intrinsically metallic owing to a high density of states at the Fermi due to a large contribution from transition metal d-orbitals.[3] They are also hydrophilic and thus easy to process. They exhibit record volumetric capacitances,[4] high optical nonlinearities, high damage thresholds for exposure to high-intensity laser light, and pronounced plasmonic effects stemming from high free carrier density [5,6]. These properties make MXenes a promising platform for optoelectronic devices in the broad spectral range from the visible to the THz.[7-9] In our previous studies, we investigated THz photoconductivity in $Ti_3C_2T_z$ and $Mo_2Ti_2C_3$ spin cast film,[9-11] and demonstrated the feasibility of a THz polarizer based on $Ti_3C_2T_z$.[12]

II. Results and discussion

Here we investigate the behavior and dynamics of photoexcitations in MXenes as a function of their chemistry (viz. transition metal) and layer structure (viz. n). We combine optical pump-THz probe spectroscopy, which can monitor transient changes in optical conductivity and properties of free carriers, and transient optical absorption, which provides access to excited state dynamics and changes in the optical absorption in the visible range. As Figs. 1a, b illustrate, optical excitation with 800 nm pulses results in a markedly different THz photoconductivity responses in $Ti_3C_2T_z$ on one hand, and $Mo_2Ti_2C_3T_z$ and Nb_2CT_z, on the other. While all three are intrinsically metallic, THz conductivity is suppressed in the former and enhanced in the latter two.

In a recent study of MXenes of different chemistries, Maleski et al. speculated that static visible – near infrared, NIR, optical properties MXenes with high concentration plasma (>10^{21} cm^{-3}), such as $Ti_3C_2T_z$, are dominated by the free carriers, while the interband transitions play a more important role in MXenes with lower free carrier concentrations.[13] We find that $Mo_2Ti_2C_3T_z$ and Nb_2CT_z exhibit transient increases in conductivity due to new photoinjected carriers that have a lifetime on the order of ~ 100 ps. On the other hand, transient suppression of THz conductivity as evidenced by the enhanced THz transmission in $Ti_3C_2T_z$ that lasts for several nanoseconds.

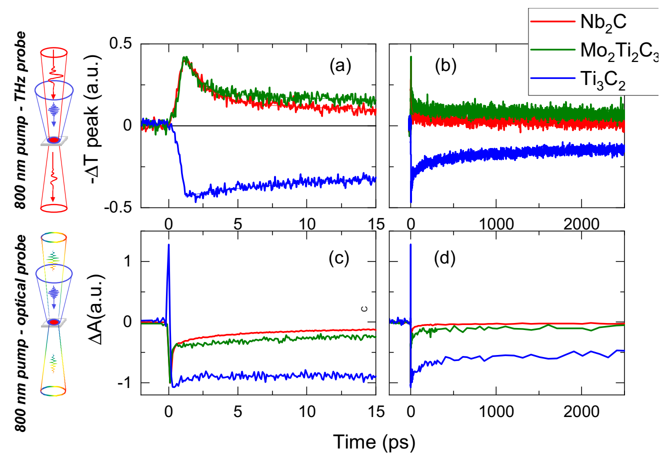

Fig. 1. (a, b) Time-resolved THz spectroscopy: transient change in conductivity after excitation with ~ 300 μJ/cm^2, 800 nm pulses in Nb-based (red), Ti-based (blue) and Mo-Ti based (green) MXenes over short (a) and long (b) time scales after excitation. (c, d) Transient optical absorption: transient absorption bleach in the visible range following 800 nm excitation. Probe wavelength was chosen at the center of absorption bleach band: 750 nm for Nb_2C, 520 nm for $Mo_2Ti_2C_3$, and 742 nm for Ti_3C_2.

To unravel the origins of this divergent behavior, we also examine transient optical absorption in response to the same (800 nm) excitation. Static optical spectra of the three MXenes exhibit broad absorption peak in the visible-NIR range.[13] Its origin is a subject of intense debate, with either interband transitions or plasmon resonance suggested as the mechanism. Figs. 1c, d shows transient optical absorption with the probe wavelengths were chosen at the center of the absorption peak for each of the MXenes. We find that in all cases, 800 nm excitation induces long-lived absorption bleach, which recovers considerably faster in $Mo_2Ti_2C_3T_z$ and Nb_2CT_z than $Ti_3C_2T_z$. The long lifetime of the optical absorption bleach raises significant doubts over the plasmonic origin of these features.

The exact mechanisms behind the observed rich palette of

MXene optoelectronic properties are yet to be fully understood. They likely arise from interplay between MXene chemistry, structure, morphology, and electronic states associated with the surface termination groups T_z. Uncovering those mechanisms will lay foundations for MXene-based THz and visible photonic devices.

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