Ultrafast dynamics of plasmons and free carriers in 2D MXenes

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Abstract: We use transient optical absorption and time-resolved terahertz THz spectroscopy to investigate photoexcitations in Ti_3C_2, $Mo_2Ti_2C_3$, and Nb_2C. Measurements reveal pronounced plasmonic effects. Monitoring them provides insights into thermal relaxation processes and low thermal conductivity.

1. Introduction

MXenes are 2D transition metal carbides, nitrides, carbonitrides or borides, with a general formula $M_{n+1}X_nT_z$, where M is a metal, X is carbon, nitrogen or boron, and n = 1, 2, 3 or 4. T_z in this formula denotes surface terminations such as –OH, –O, and/or –F, that are responsible for MXenes being easily dispersed in water. Most of currently known MXenes are intrinsically metallic and exhibit record volumetric capacitances and conductivities; several of them have also demonstrated significant optical nonlinearities and high laser damage thresholds [1]. Their unique optical properties offer promise of applications in electromagnetic interference, EMI, shields, optical and THz switches, polarizers, modulators, wavelength convertors, and detectors[2-6]. The optical properties of MXenes are determined by a complicated interplay between the free carriers, interband transitions, and plasmon resonances in the visible and near-IR spectral ranges [7,8]. MXene plasmonic properties have been suggested as underlying mechanisms responsible for efficient conversion of light to heat, saturable optical absorption and high performance photodetectors [5, 9-11].

In our recent paper, we studied photoexcitations in three different members of MXene family, Ti_3C_2, $Mo_2Ti_2C_3$, and Nb_2C, using transient optical absorption, TA, and the time-resolved THz spectroscopy (TRTS) measurements. Correlating the effects of photoexcitation with 400 nm and 800 nm laser pulses on the optical properties in the visible and near-IR range, where plasmon features are observed, with those in the THz range, where the free carrier absorption dominates, allows us to unravel the complicated photoinduced processes in these materials [12].

2. Results and Discussion

All three studied MXenes exhibit an optical absorption peak in the visible or near-infrared range: at 742 nm in Ti_3C_2, at 520 nm in $Mo_2Ti_2C_3$ and at 730 nm in Nb_2C. In the case of Ti_3C_2, this feature has been previously assigned to a localized surface plasmon resonance, or LSPR. We find that this absorption resonance displays the same qualitative ultrafast transient optical properties in all three materials. Specifically, regardless of the photon energy (1.55 eV vs 3.1 eV), and regardless of whether the excitation is near-resonant or off-resonant with respect to the static absorption peak, photoexcitation results in a sustained absorption decrease centered at the energy of this peak (Fig. 1). We attribute this behavior to transient optically-induced broadening of the LSPR peak that presents as plasmon bleaching (PB) in the TA spectra and kinetic traces. We therefore conclude that the LSPR effects govern visible-near-IR optical response in these materials. The transient bleach of plasmon modes in response to optical excitation results from the creation of a non-equilibrium hot carrier distribution over sub-100 fs time scales, followed by lattice heating by electron-phonon interactions. As the lattice cools due to thermal diffusion to the surroundings, PB recovers. Monitoring the recovery of PB provides insight into thermal relaxation processes.

Here, we observe PB relaxation that is considerably slower than in noble metals [12]. It proceeds over nanoseconds time scales in Ti_3C_2, somewhat faster in $Mo_2Ti_2C_3$, and finally over ~ 110 ps in Nb_2C. We note here that PB recovery is the slowest in the MXene with the highest carrier density, Ti_3C_2, as determined by the THz spectroscopy, and the fastest in Nb_2C, which is found to have negligible intrinsic carrier density and transient photoexcited carrier density that decays over comparable, ~ 100 ps, time scales. Earlier reports suggested that room temperature thermal

conductivity in Ti_3C_2 (2.84 W m^{-1} K^{-1}) is much lower than in noble metals, and heat is dissipated predominantly by low frequency phonons [13].

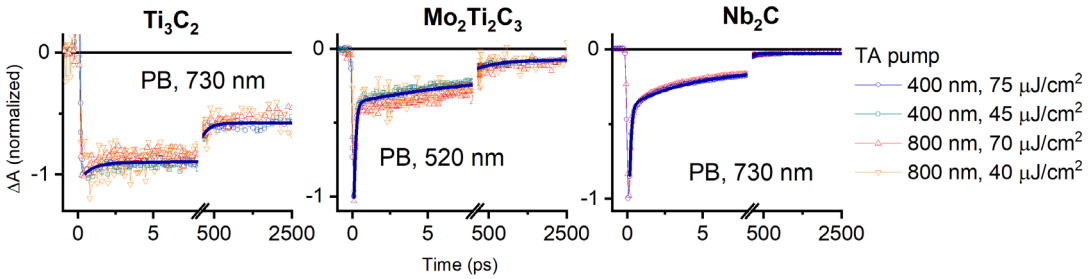

Fig. 1. Normalized TA kinetic traces for Ti_3C_2, $Mo_2Ti_2C_3$, and Nb_2C). Pump wavelength and fluence values shown in the legend, and TA probe wavelengths (plasmon resonances) are indicated in each panel.

Theoretical study has also found that in Nb_2C, unusually strong electron-phonon scattering results in a large reduction in lattice thermal conductivity [14]. We therefore propose that the observed unusually slow recovery of plasmon damping in MXene films following optical excitation is a result of low thermal conductivity. High carrier-phonon scattering leads to rapid and efficient localized heating of the crystal lattice and limits thermal conductivity, as low-frequency acoustic phonons are strongly scattered not only off each other, flake edges and defects, but also by free carriers.

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4. References

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