Direct Observation of Electron-Vibration Coupling at MXene-Solvent Interface

Yan-jun Xu\textsuperscript{a,b}, He-yuan Liu\textsuperscript{a,b}, Hai-long Chen\textsuperscript{a,c}\textsuperscript{*}

\textsuperscript{a} The Laboratory of Soft Matter Physics, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
\textsuperscript{b} School of Physical Science, University of Chinese Academy of Sciences, Beijing 100049, China
\textsuperscript{c} Songshan Lake Materials Laboratory, Dongguan 523808, China

(Dated: Received on August 14, 2021; Accepted on September 7, 2021)

MXenes, a new family of two-dimensional (2D) materials, have received extensive interest due to their fascinating physicochemical properties, such as outstanding light-to-heat conversion efficiency. However, the photothermal conversion mechanism of MXenes is still poorly understood. Here, by using femtosecond visible and mid-infrared transient absorption spectroscopy, the electronic energy dissipation dynamics of MXene (Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}) nanosheets dispersed in various solvents are carefully studied. Our results indicate that the lifetime of photoexcited MXene is strongly dependent on the surrounding environment. Especially, the interfacial electron-vibration coupling between the MXene nanosheets and the adjacent solvent molecules is directly observed following the ultrafast photoexcitation of MXene. It suggests that the interfacial interactions at the MXene-solvent interface play a critical role in the ultrafast energy transport dynamics of MXene, which offers a potentially feasible route for tailoring the light conversion properties of 2D systems.

Key words: MXene, Ultrafast spectroscopy, Photothermal conversion, Electron-vibration coupling

I. INTRODUCTION

As a new series of promising two-dimensional (2D) materials [1], MXenes have been found potential applications in many fields, such as battery technology, energy storage [2, 3], desalination [4], wastewater treatment [5], transducer [6, 7] and medicine [8]. Very recently, the strong light-harvesting properties of MXenes have been demonstrated to be highly favorable for light-to-heat conversion applications [9–11], including solar steam generation, solar photothermal electrode, photothermal therapy, light-driven actuator, and so on [8, 12–16]. For instance, Wang’s group reported nearly 100% internal light-to-heat conversion efficiency of Ti\textsubscript{3}C\textsubscript{2}, demonstrating that MXene can convert light energy into water steam for practical use of solar energy.
by virtue of its wonderful photothermal characteristics [15]. Lin et al. reported the use of Nb$_2$C MXene in the NIR window for efficient in vivo photothermal ablation of mouse tumors [16]. Despite such recent progress, the investigation of photothermal properties of MXenes is still in the primary stage. As a consequence, the photothermal conversion mechanism of MXenes, especially at the molecular level, remains poorly understood.

With 2D morphology, hydrophilicity and rich functional groups (generally -OH, -O, and -F) at the surface of MXene [17], the photothermal conversion pathways in MXenes are in general greatly modulated by their interfacial environment [18]. Experimentally revealing the energy migration channels and the interfacial interaction behaviors at MXene surfaces is of significant importance for uncovering the photothermal conversion mechanism. We have demonstrated that the interfacial interaction is crucial for effective hydrogen bond formation on MXene surfaces to promote flash energy transport at MXene-solvent interface [19]. A hydrogen bond mediated energy transport channel as fast as 7 ps in MXene aqueous solution was clearly observed with the aid of femtosecond transient absorption (TA) spectroscopy. Li et al. studied the ultrafast flash energy conductance at MXene-surfactant interface, and found that cetrimonium bromide molecules could effectively block the energy transport from MXene to water due to strong coulomb interaction between the surface molecules and MXene [20]. These works also confirmed that the femtosecond TA spectroscopy is an effective method to monitor the photothermal conversion pathways at MXene-solvent interface. However, a direct experimental evidence supporting the strong MXene-solvent interaction is still lacking.

In this work, we perform the femtosecond TA spectroscopy in both visible and mid-infrared (MIR) spectral regions to study the energy transport dynamics at MXene-solvent interface in various environments. The samples are Ti$_3$C$_2$Tx MXene nanosheets dispersed in different solvents, including water, DMF and DMSO. Here, the MIR TA spectra can help us to directly monitor the response of vibrational modes in solvent molecules upon the ultrafast photoexcitation of MXene nanosheets. Our results show that the lifetime of photoexcited MXene is strongly dependent on the surrounding environment. The MIR TA spectra further reveal the existence of strong interfacial electron-vibration coupling between the MXene nanosheets and the adjacent solvent molecules, suggesting that the flash energy transport from Ti$_3$C$_2$Tx MXene to the surroundings can be effectively tuned by the interfacial interaction.

II. MATERIALS AND METHODS

A. Sample preparation

The MXene samples are commercial few-layer Ti$_3$C$_2$Tx nanosheets dispersed in water and organic solvents (DMF and DMSO). The preparation methods have been widely reported [11, 21, 22]. In brief, Ti$_3$AlC$_2$ was first corroded by fluoride ions at room temperature, then centrifuged and freeze-dried to obtain Ti$_3$C$_2$Tx powder. The water-soluble suspension of Ti$_3$C$_2$Tx MXene can be obtained by dispersing the MXene powder in water followed by continuous centrifugation. The samples of Ti$_3$C$_2$Tx MXene in organic solvent were prepared by tuning the microenvironment of the MXene. The MXene powder was first added into the tetrabutylammonium hydroxide (TBAOH) solution which was used as an intercalant and surface modifier, then followed by stirring the solution at room temperature for intercalation. Subsequently, it was washed with ethanol to remove the excess TBAOH, and then the organic solvent such as DMF or DMSO was added into the resultant precipitate. The Ti$_3$C$_2$Tx MXene could be well dispersed in the organic solvent by shaking the above mixture until the precipitate was completely dispersed. Finally, we obtained the DMF or DMSO solution of MXene by collecting the uniform supernatant after the centrifugation.

The concentrations of MXene solutions used for the visible and the MIR optical experiments were all controlled at 0.15 mg/mL and 5 mg/mL, respectively.

B. Steady-state characterizations

Atomic force microscopy (AFM) was conducted by Bucker Dimension Edge, with MXene flakes coated on a silicon substrate. X-ray photoelectron spectroscopy (XPS) measurement was performed on an X-ray photoelectron spectrometer (ESCALAB Xi+, Thermo Scientific) using the Al K$_\alpha$ monochromatic beam (1486.6 eV) with an input power of 150 W. Steady-state absorption spectrum was collected with a home-made spectrophotometer. Fourier transform infrared (FTIR) spectra were collected using an FTIR spectrometer (VERTEX 70v, BRUKER).
C. Femtosecond visible and MIR TA spectroscopy

The femtosecond visible TA spectroscopy was performed by using a femtosecond amplifier laser system (Spitfire Ace, Spectra Physics) with a duration of \( \sim 100 \text{ fs} \), a center wavelength of 800 nm and a repetition rate of 2 kHz. The output of laser was split into two beams. The first beam was directly used as the pump pulses. The second beam was focused on a CaF\(_2\) plate to produce the white-light supercontinuum as the visible probe pulses. The motorized delay stage was used to control the time delay between the pump and the probe beam, both of which focused onto the sample and overlapped in space. After passing through the sample, the probe light was collected by an optical fiber spectrometer (AvaSpec-ULS2048CL-EVO, Avantes) to record the excitation-induced absorption change of the sample.

The femtosecond MIR TA spectroscopy was performed by using a femtosecond amplifier laser system (Spitfire Ace, Spectra Physics) with a duration of \( \sim 35 \text{ fs} \), a center wavelength of 800 nm, and a repetition rate of 1 kHz. The experimental setup is roughly similar to that of visible TA spectroscopy. Here, the probe beam was replaced by an ultra-broadband supercontinuum pulse covering almost the whole mid-IR region, which was generated by focusing 800 nm fundamental light and 400 nm second harmonic simultaneously on air [23, 24]. After passing through the sample, the MIR probe light was collected by a liquid-nitrogen-cooled mercury-cadmium-telluride array detector after frequency resolved by a spectrograph (iHR 320, HORIBA JobinYvon).

III. RESULTS AND DISCUSSION

A. Characterizations of MXene nanosheets

MXenes generally have a formula of \( M_{n+1}X_nT_x \) (\( n=1, 2, \) or 3), where \( M \) is an early transition metal, \( X \) is carbon or nitrogen, and \( T_x \) is the surface functional group such as -O, -OH, and -F. These abundant hydrophilic groups at the surface endow MXenes with highly hydrophilic properties [25] and also promote the formation of hydrogen bonds with surrounding water or ethanol molecules [19]. In this work, the typical MXene Ti\(_3\)C\(_2\)T\(_x\) was chosen to investigate the interaction between the MXene and different solvent molecules. The AFM measurement of MXene flakes indicates that their thicknesses are mainly around 3 nm, as depicted in FIG. 1(a). It was reported that the thickness of a single-layer MXene flake is about 1 nm [26], confirming that the MXene nanosheets we have measured are few layered. The XPS spectrum displayed in FIG. 1(b) characterizes the existence of four major elements Ti, C, F, and O in MXene, which is in accord with a previous report [11]. The steady-state absorption spectra shown in FIG. 1(c) and FIG. S1 (see Supplementary materials) indicate that the MXene solution exhibits an absorption peak centered at around 760 nm, which can be attributed to the plasmonic mode [27]. In the following ultrafast spectroscopic measurements, the central wavelength of the pump light is all fixed at 800 nm for the photoexcitation of MXene nanosheets. The FTIR spectra of MXene in different solvents are shown in FIG. 1(d). Since the concentration (5 mg/mL) of MXene solutions is not too large, the FTIR spectral feature is dominated by the vibrational peaks of solvent molecules. For example, the peak centered at 1649 cm\(^{-1}\) in aqueous solution is due to the bending mode of water molecules; in DMF, the peak centered at 1677 cm\(^{-1}\) is attributed to the stretching vibration of the C=O bond; in DMSO, the peak at 1050 cm\(^{-1}\) is due to the stretching vibration of the S=O bond.

B. Solvent dependent energy transport dynamics

To reveal the energy transport dynamic of MXene in different solvents, the femtosecond visible TA spectroscopy was first performed. The pump light centered at 800 nm was used to excite MXene nanosheets, with the pump fluence of \( \sim 200 \text{ mJ/cm}^2 \). As depicted in FIG. 2(a), the TA spectrum of the MXene aqueous solution after photoexcitation is mainly composed of a negative peak centered at 760 nm and a positive broadband signal ranging from 450 nm to 650 nm. The negative peak which is close to the plasmonic mode of MXene (see FIG. 1(c)) is attributed to the photobleaching of the absorption band due to the 800 nm photoexcitation. The positive band is the photoinduced absorption (PA) signal. The similar phenomenon has been reported in the previous work [19]. The TA spectra for the MXene in DMF and in DMSO solvents are presented in FIG. 2(b) and (c), respectively, both of which have the similar feature to that for the MXene aqueous solution.

FIG. 2(d) compares the temporal evolutions of excitation-induced absorption change for three different MXene solutions, with the probe wavelength fixed...
FIG. 1 (a) AFM image of Ti$_3$C$_2$Tx MXene flakes on a silicon substrate. The inset shows the step-height profile. (b) XPS spectrum of Ti$_3$C$_2$Tx MXene. (c) Steady-state absorption spectrum of Ti$_3$C$_2$Tx MXene in aqueous solution. (d) FTIR spectra of MXene in different solvents.

FIG. 2 Waiting time dependent visible TA spectra of MXene dispersed (a) in water, (b) in DMF, and (c) in DMSO after photoexcitation at 800 nm. (d) Normalized TA dynamics probed at 520 nm for different MXene solutions. Dots are data, and curves are multi-exponential fitting with the consideration of instrument response function (~150 fs).

at 520 nm. The normalized TA dynamics probed at 650 nm for different solutions are also provided in FIG. S2 (Supplementary materials), where a similar trend can be observed. We have demonstrated that these dynamics can be roughly described in three stages: first, electron-electron thermalization (~100 fs); second, electron-phonon thermalization (1–2 ps); and third, coupling to the environment (interfacial energy transport). The lifetime for the third stage is strongly dependent on the surrounding environment of MXene, which can be even larger than 10 ns for the MXene nanosheets without contact with any solvent molecules [19]. Here,
for the MXene dispersed in different solvents, the interfacial energy transport dynamics associated with the third stage can only last hundreds of picoseconds. All these transport processes can be described by two time constants, which are fitted as 6.3±0.2 ps (78%) and 110±10 ps (22%) for the aqueous solution, 26±2 ps (54%) and 200±20 ps (46%) for the DMF solution, and 19±4 ps (41%) and 110±10 ps (59%) for the DMSO solution. We have demonstrated that the significantly shortened lifetime for the MXene aqueous solution can be attributed to the formation of hydrogen bonds on MXene surfaces that provide rapid energy transport channels [19]. In that work, we also performed the same measurements on the MXene in ethanol solution and PVA mixture, all of these results indicated that the environment at MXene surfaces had great impact on the interfacial energy transport dynamics. Here, for the MXene nanosheets dispersed in DMF or DMSO, the solvent molecules have much weaker hydrogen bond forming abilities. The result indicates that the interfacial interaction aside from the hydrogen bonding can also play a dominant role in the ultrafast energy transport dynamics of MXene, despite that with a relatively slower transport rate.

C. Interfacial electron-vibration coupling

Since the lifetime of photoexcited MXene strongly depends on the type of solvent, the interfacial interaction between the MXene nanosheets and the solvent molecules is expected to play a critical role. To directly monitor the response of vibrational modes in solvent molecules upon the photoexcitation of MXene, the femtosecond MIR TA spectroscopy was further performed on different MXene solutions. Specifically, the 800 nm pump laser with the fluence of ~500 μJ/cm² was used to excite the MXene, and then the excitation-induced MIR absorption changes of these nanosheets as well as the solvent molecules were monitored with the MIR supercontinuum pulses.

FIG. 3(a) presents the MIR TA spectra of MXene aqueous solution at three typical time delays, all of which are featured with broadband negative photo-bleaching signals. This feature arises from the photoinduced absorption change of MXene nanosheets in the MIR region. One possible reason is that the presence of -OH and -F groups on the surface can convert metal MXene into semiconductors, with bandgaps of around 0.05 eV and 0.1 eV, respectively [1]. For the TA spectrum of a typical semiconductor, a continuum band bleaching signal due to band filling can be commonly observed in the spectral region above the bandgap [28]. More importantly, it is worth noting that a negative peak centered at 1640 cm⁻¹ can be clearly observed in addition to the broadband photobleaching background, which is close to the bending mode of water molecules (see FIG. 1(d)). This phenomenon will be discussed in detail later. The MIR TA spectra for DMF and DMSO solutions are presented in FIG. 3 (b) and (c), respectively. The similar broadband photobleaching feature due to the excitation of MXene nanosheets is still observed. The temporal evolutions of excitation-induced absorption change for different MXene solutions are compared in FIG. 3(d), with the probe wavenumber fixed at 1600 cm⁻¹. All the dynamics can be well fitted by the triple-exponential function (the curves in FIG. 3(d)). Apart from the initial fast decay (~100 fs), the remaining two time constants are obtained as 5.7±0.2 ps (80%) and 80±10 ps (20%) for the aqueous solution, 19±5 ps (43%) and 150±30 ps (57%) for the DMF solution, and 18±2 ps (47%) and 130±20 ps (53%) for the DMSO solution, respectively. These results are consistent with those measured in the visible region (see FIG. 2(d)), confirming that the temporal evolutions of MIR signal are also related to the interfacial energy transport dynamics of photoexcited MXene.

Furthermore, we repeated the MIR measurements to focus on the spectral regions related to some specific vibrational modes of solvent molecules. FIG. 4 (a) and (b) compare the TA spectra of different MXene solutions in the MIR regions at around 2950 cm⁻¹ and 1680 cm⁻¹, respectively. In addition to the broadband negative photobleaching backgrounds contributed by MXene, some negative peaks also clearly appear in the TA spectra, which correspond well to the absorption peaks in corresponding FTIR spectra (black lines in FIG. 4 (a) and (b)). For example, in water, there is a broad negative peak centered at 1640 cm⁻¹, which is close to the bending mode of water molecules; in DMF, there is a narrow negative peak at around 1690 cm⁻¹ and two negative peaks at around 2900 cm⁻¹, which can be assigned to the response of C=O stretching mode and CH₃ stretching modes, respectively; in DMSO, there are negative peaks located at around 2950 cm⁻¹, which can be attributed to the response of CH₃ stret-
FIG. 3 MIR TA spectra at three typical time delays for the MXene dispersed (a) in water, (b) in DMF, and (c) in DMSO after photoexcitation at 800 nm. (d) Normalized TA dynamics probed at 1600 cm\(^{-1}\) for different Ti\(_3\)C\(_2\)Tx MXene solutions. Dots are data, and curves are multi-exponential fitting with the consideration of instrument response function (∼150 fs).

FIG. 4 Comparing the MIR TA spectra (red lines) at 0.1 ps with corresponding FTIR spectra (black lines) in spectral regions at (a) ∼2950 cm\(^{-1}\) and (b) ∼1680 cm\(^{-1}\) for different MXene solutions. (c) Temporal evolutions of excitation-induced absorption change for three typical vibrational modes (red lines) and their adjacent photobleaching backgrounds (black lines).

DOI:10.1063/1674-0068/cjcp2108135  ©2021 Chinese Physical Society
hiching modes in DMSO molecules (since the signal for the DMSO solution is not clear enough, the corresponding spectrum shown in FIG. 4(a) was obtained by averaging the TA data of DMSO solution from 0.5 ps to 5 ps).

According to the principles of transient vibrational signal generation [29, 30], these negative peaks related to different vibrational modes generally have three possible origins: (i) energy transfer from the electronic state of MXene to the vibrational state of solvent molecules, (ii) the laser heating effect, and (iii) the electron-vibration coupling at MXene-solvent interface. At first, we can consider the first two possibilities. Regardless of whether it is energy transfer or heating effect, an additional dynamics related to energy (or heat) transfer process should exist in the TA spectra. It is generally observed as a gradual increase of signal intensity with a time constant on the picosecond time scale. To verify this, we have compared the temporal evolutions of these negative peaks with their adjacent photobleaching backgrounds for each MXene solution. The dynamics associated with three typical vibrational modes are depicted in FIG. 4(c). The result indicates that the temporal evolution for each vibrational mode associated signal is almost identical to that for its adjacent photobleaching background, and no extra rising or decay dynamics can be observed. As a consequence, the first two possibilities can be ruled out here, and it is very likely that the appearances of these transient vibrational signals are induced by the existence of strong electron-vibration coupling between the excited electronic state of MXene and the vibrational state of solvent molecules. The almost identical temporal evolution feature between these coupling signals and corresponding photobleaching backgrounds, which are related to the interfacial energy transport dynamics of photoexcited MXene, can further confirm that the interfacial interactions at the MXene-solvent interface should play a critical role in the ultrafast energy transport dynamics of MXene.

In a previous study on 2D MoS$_2$ nanosheets, the rapid electronic energy dissipation of MoS$_2$ through a direct coupling to the low-frequency vibration modes of the surrounding solvent was also observed [31]. Moreover, the interfacial electron-phonon coupling has been widely reported as a mechanism that directly impacts carrier transport in 2D materials [32, 33]. Specially, it was found that in some 2D material heterostructures, the coupling between the electronic transitions of 2D materials and the phonons from the dielectric substrates are particularly strong [34, 35]. Therefore, the existence of strong interfacial electron-vibration coupling between 2D MXene and adjacent solvent molecules can offer a potentially viable route for tailoring the light conversion properties of these materials. The MIR TA spectra displayed in FIG. 4 (a) and (b) also suggest that the interfacial electron-vibration coupling between the MXene and the solvent molecules is not mode-selective. Considering the Ti$_3$C$_2$T$_x$ MXene is a metallic material or a semiconductor with the bandgap less than 0.1 eV, it offers the possibility of the resonance energy transfer between the excited electronic states of MXene and the solvent vibrational modes. However, since the vibrational lifetime of solvent molecules (~1–2 ps) is generally much shorter than the interfacial energy transport time (tens to hundreds ps), the resonance energy transfer process is difficult to be directly monitored. This issue needs to be addressed in future studies.

IV. CONCLUSION

In summary, both the visible and MIR femtosecond TA spectroscopies have been employed to study the electronic energy dissipation dynamics of Ti$_3$C$_2$T$_x$ MXene nanosheets dispersed in three kinds of typical solvents. The interfacial energy transport dynamics for each MXene solution is successfully monitored, which is found to be strongly dependent on the type of solvent. Further, the MIR TA measurement confirms the existence of strong interfacial electron-vibration coupling between the MXene nanosheets and the solvent molecules. This result suggests that the flash energy dissipation from Ti$_3$C$_2$T$_x$ MXene to surrounding environment can be effectively tuned by the interfacial interaction, providing important insights and experimental basis into the future photothermal applications with MXene and other 2D materials.

Supplementary materials: Steady-state absorption spectra of MXene in different solvents and TA dynamics probed at 650 nm for different MXene solutions are shown.

V. ACKNOWLEDGMENTS

This work was supported by the National Key Research and Development Program of China
for the XPS measurements.


9. Z. Huang, X. Cui, S. Li, J. C. Wei, P. Li, Y. Wang, and C. S. Lee, Nanophotonics 9, 2233 (2020).