Photoinduced two-step insulator–metal transition in Ti₄O₇ via ultrafast time-resolved optical reflectivity

Xu-Chen Nie¹, Hai-Ying Song¹, Xiu Zhang¹, Shi-Bing Liu¹, Fan Li², Lili Yue³, Jian-Qiao Meng⁴, Yu-Xia Duan⁵, Lin Zhao⁶, and Hai-Yun Liu¹*

¹Strong-field and Ultrafast Photonics Lab, Institute of Laser Engineering, Beijing University of Technology, Beijing 100124, P. R. China
²Department of Chemistry and Chemical Engineering, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, P. R. China
³College of Applied Sciences, Beijing University of Technology, Beijing 10124, P. R. China
⁴Hunan Key Laboratory of Super-microstructure and Ultrafast Process, School of Physics and Electronics, Central South University, Changsha, Hunan 410083, P. R. China
⁵School of Physics and Electronics, Central South University, Changsha, Hunan 410083, P. R. China
⁶National Laboratory for Superconductivity, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P. R. China

*e-mail: haiyun.liu@bjut.edu.cn

Received June 22, 2018; accepted July 22, 2018; published online August 7, 2018

We report on the systematic investigation of hot carrier dynamics in Ti₄O₇ by ultrafast time-resolved optical reflectivity. We find the transient indication for its two-step insulator–metal (I–M) transition, i.e., from the long-range ordered bipolaron low-temperature insulating phase to the disordered bipolaron high-temperature insulating phase at Tc1 and to the free-carrier metallic phase at Tc2. Our results reveal that photoexcitation can effectively reduce both Tc1 and Tc2 by increasing the pump fluence, allowing the light-control of the I–M transition. We address a phase diagram that provides a framework for the photoinduced I–M transition and helps the potential use of Ti₄O₇ for photoelectric and thermoelectric devices.

Photoinduced two-step insulator–metal transition in Ti₄O₇ via ultrafast time-resolved optical reflectivity

T

The insulator–metal (I–M) transition has attracted considerable interest over the past half century in condensed-matter physics,¹–³ however, the mechanism of which remains controversial.⁴ Various scenarios have been proposed, including the opening of a gap due to spectral weight transfer,⁵ Anderson localization of electrons induced by lattice disorder,⁶,⁷ and polaron self-trapping driven by electron–phonon (e–ph) interactions.⁷ In addition to the control of the phase transition through equilibrium methods, such as temperature, chemical-doping, and pressure variation, the photoinduced I–M transition in nonequilibrium states is of great interest for the study of ultrafast physics and the light-control of electronic properties.⁸ For example, in semiconductor GaAs, a transient I–M transition can be induced by the interplay between free carriers and excitons, accompanied by a sign reverse of time-resolved reflectivity changes.⁹ The photoinduced I–M transition in strongly correlated systems caused by implementing ultrafast photoincination through the melting of the charge-density-wave (CDW) order in low-dimensional CDW materials has attracted growing interest,¹⁰–¹² along with the resonant phonon-driven melting of the orbital or magnetic order in magnetoresistive manganites.¹³,¹⁴ etc.

Titanium oxide Ti₄O₇ is a member of the transition-metal oxides (TMOs) with the Magnéli phase, which hosts a triclinic structure and a characteristic two-step I–M transition accompanied by large reflectivity and heat-capacity changes.¹⁵–¹⁹ It has one 3d electron per two Ti ions, allowing two possible valence states of Ti⁴⁺(3d⁰) and Ti⁴⁺(3d⁰). As depicted in Fig. 1(a), in the high-temperature metallic (M) phase, Ti ions have an uniform valence state of +3.5, and the 3d electrons are delocalized and contribute to the electrical conductivity. Below 150 K (Tc₂), Ti ions take alternative valence state of Ti⁵⁺ and Ti⁴⁺, and the 3d electrons are localized to form covalently bonded Ti³⁺–Ti³⁺ pairs, which can be considered as bipolarons.¹⁹,²⁰ For the low-temperature insulating (LI) phase below 130 K (Tc₁), well-ordered Ti³⁺–Ti³⁺ pairs appear, while this long-range order vanishes in the high-temperature insulating (HI) phase (130 < T < 150 K).¹⁷–²⁷ Titanium dioxide has been widely used in photocatalysis in rechargeable batteries.²⁸,²⁹ Resistive switching in titanium dioxide has attracted considerable attention owing to its potential application in nonvolatile memory devices called resistance random access memory.³⁰,³¹ Recently, optical-pump terahertz-probe measurements have revealed the photoinduced I–M transition in Ti₄O₇ by monitoring the dynamic relaxation on the timescale of tens of picoseconds (ps).³² However, systematic investigations of the ultrafast dynamics on the
subpicosecond scale, the photoinduced I–M via a two-step procedure, and phase diagrams are still lacking.

Ultrafast time-resolved optical reflectivity has proven to be an effective method for tracking the hot carrier dynamics in semiconductors\(^9\) and correlated electron materials,\(^{12,33}\) including cuprate high-\(T_c\) superconductors\(^{34-36}\) and many other transition-metal oxides.\(^{37}\) The initially photoexcited hot carriers thermalize and redistribute primarily through electron–electron (e–e) scattering within tens of femtoseconds (fs), which is comparable to the temporal resolution, and afterwards they temporally accumulate above the gap, accompanied by a relaxation bottleneck and cooling to the lattice temperature predominantly via the e–ph scattering.

In this paper, we present systematic studies on the hot carrier dynamics in polycrystalline \(\text{Ti}_4\text{O}_7\) using ultrafast time-resolved optical reflectivity. Our results reveal that with increasing temperature, the oxide undergoes a two-step phase transition from the ordered bipolaron L phase to the disordered bipolaron HI phase at \(T_{c1}\) and to the free-carrier M phase at \(T_{c2}\), accompanied by clear slope changes in the transient amplitude and relaxation times. In addition, our study clearly shows that both \(T_{c1}\) and \(T_{c2}\) decrease with the increase of the pump fluence, indicating that photoexcitation is effective for inducing the I–M transition in this system. The possible mechanism of the photoinduced I–M transition is discussed.

The ultrafast time-resolved optical reflectivity measurements were performed on polycrystalline \(\text{Ti}_4\text{O}_7\) using a pump–probe setup, in which optical pulses with a temporal duration of 35 fs and a central wavelength of 800 nm were produced by a regeneratively amplified Ti:sapphire laser system operating at a repetition rate of 1 kHz.\(^9,36\) The mirror-like sample surface was obtained via mechanical polishing.

The pump beam was focused on the sample at near-normal incidence with a spot diameter of \(\sim 0.4\) mm, and the probe spot diameter was \(\sim 0.2\) mm, as measured by imaging the spots in the focal plane of a charge-coupled device camera, ensuring an excellent pump–probe overlap. With the pump beam modulated by a chopper, the reflected probe signal was focused onto a Si-based detector, which was connected to a lock-in amplifier, where the photoinduced transient reflectivity variation \(\Delta R/R\) was recorded with a sensitivity on the order of \(10^{-6}\). The temporal evolution of the pump-induced change in the probe reflectivity \((\Delta R/R)\) was measured by scanning the delay time between the pump and probe pulses using a motorized delay line. To perform the temperature-dependent measurements, the sample was mounted on a cryostat with a temperature sensor embedded nearby, allowing precise control of the temperature in the range of 5–300 K. The pump fluence \((F)\) was tunable between 70 and 430 \(\mu\)J/cm\(^2\) by using neutral-density filters, and a probe fluence of 4 \(\mu\)J/cm\(^2\) was chosen to minimize the steady-state heating and maximizing the signal-to-noise ratio.

Figure 1(b) displays the time-resolved differential reflectivity \(\Delta R/R\) of polycrystalline \(\text{Ti}_4\text{O}_7\) as a function of the delay time at three representative temperatures: 80, 140, and 180 K, which characterize LI, HI, and M phases, respectively. At all temperatures, the photoexcitation causes a sharp edge around time zero and an abrupt drop at 0.1 ps, corresponding to the very fast thermalization process due to e–e scattering, which is difficult to resolve with our temporal resolution.

More interestingly, the following sub-picosecond recovery shows strong \(T\)-dependent behavior: both the amplitude and relaxation increase with the decrease of the temperature. Obviously, owing to the opening of the bandgap and the suppression of any mid-gap states, more hot carriers are accumulated around the bottom of the conduction band immediately after the thermalization process, resulting in an enhanced amplitude and relaxation bottleneck. As indicated by the black curves, the decay is well-described by a single-exponential decay function \(\Delta R/R = Ae^{-t/\tau} + A_0\) on a ps timescale, where the amplitude \(A\) is proportional to the photoexcited carrier density, \(\tau\) is the characteristic relaxation, and \(A_0\) describes far slower equilibration processes outside of the period of the measurement, such as heat diffusion, corresponding to the long-lived reflectivity plateau, as depicted in the inset.

To quantitatively identify the relationship between the hot carrier dynamics and the phase transitions, in Fig. 2, we plot the amplitudes \(A\) and the relaxation times \(\tau\) extracted from single-exponential decay fits with respect to the temperature at various pump fluences ranging from 70 to 430 \(\mu\)J/cm\(^2\). As clearly shown in Fig. 2(a), at a low pump fluence of 70 \(\mu\)J/cm\(^2\), both the magnitudes \(A(T)\) and the relaxation time \(\tau(T)\) show slope changes around \(T_{c1} = 130\) K and \(T_{c2} = 150\) K, in agreement with the LI–HI and HI–M phase-transition temperatures.\(^{21-24}\) The light red stripes in the region from \(T_{c1}\) to \(T_{c2}\) imply that the gap opening might possess a linear relationship with the temperature. More interestingly, we observe that both \(T_{c1}\) and \(T_{c2}\) decrease with the increase of the pump fluence \(F\), indicating a significant I–M phase transition caused by photoexcitation. At \(F = 430\) \(\mu\)J/cm\(^2\), \(T_{c1}\) and \(T_{c2}\) are as low as 80 and 100 K, respectively, as shown in Fig. 2(d).

Figure 3(a) shows a schematic of the photoexcitation and probing via pump and probe pulses. The transient reflectivity change \(\Delta R/R\) arises from the absorption of the photoexcited electrons. Here, \(\Delta R/R\) is proportional to the density of the photoexcited electrons \((n_p)\) with across-gap relaxation \(\tau.\)\(^{33,36}\) As such, both \(n_p\) and \(\tau\) depend strongly on the gap properties, such as the gap size. Figure 3(b) illustrates the electronic structure associated with the phase transitions. In the free-carrier M phase above \(T_{c2}\), the delocalization of Ti 3d electrons contributes to the electronic density of states (DOS) around the Fermi level \((E_F)\), as well-observed both experimentally\(^{16}\) and theoretically.\(^{23,27}\) In the HI phase \((T_{c1} < T < T_{c2}), a\) disorganized bipolaron feature forms owing to the Anderson localization of the 3d electrons induced by lattice disorder, resulting in a suppressed DOS near \(E_F\). Then, by further cooling to the LI phase \((T < T_{c1}), well-ordered bipolarons appear owing to the inter-site Coulomb interaction, accompanied by the opening of an insulating gap \((\sim 100\) meV\) driven by spectral weight transfer, which can be observed in photoemission spectroscopy measurements.\(^{18,24}\)

A polaron is a fermionic quasiparticle formed by an electron coupled with a virtual cloud of phonons (distortions), which was first proposed by Landau in 1933,\(^{38}\) for which the mobility of the electron mobility decreases and the effective mass increases. It can be described by the Fröhlich model in the weakly interacting regime.\(^{39}\) When two polarons are close together, they can further reduce their energy by sharing the same distortions, leading to an effective attraction.
between the polarons. If the interaction is sufficiently large, this attraction gives rise to a bound bipolaron. As illustrated in Fig. 3, we can interpret our photoexcited I–M transition results as follows: photoexcitation generates a large number of free carriers, which can suppress bipolaron ordering by screening the inter-site Coulomb interaction and force the insulating gap to close, inducing a transition from the ordered bipolaron LI phase to the disordered bipolaron HI phase even at lattice temperatures below $T_{c1}$. By further increasing the pump fluence, photoexcitation leads to the dissociation of the bipolarons through the delocalization of Ti 3d electrons, resulting in transient metallic properties, analogous to the transition from the disordered bipolaron HI phase to the free-carrier M phase at $T_{c2}$. Therefore, one can precisely control $T_{c1}$ and $T_{c2}$ via the careful selection of the pump fluences.

Figure 4 presents the phase diagram of Ti$_4$O$_7$, which was obtained by extracting the transition temperatures $T_{c1}$ and $T_{c2}$ from our results in Fig. 2. The phase diagram consists of three regimes: (1) Above $T_{c2}$, a free-carrier metallic state; (2) Between $T_{c1}$ and $T_{c2}$, a disordered bipolaron HI state; and (3) Below $T_{c1}$, a well-ordered bipolaron LI state. The $F$ dependence of $T_{c1}$ and $T_{c2}$ allows light-control of the I–M transition.
In summary, we presented detailed time-resolved optical reflectivity measurements of polycrystalline titanium oxide TiO$_2$. Our results provide clear evidence for the photo-induced two-step I–M transition from the ordered bipolaron LI phase to the disordered bipolaron HI phase and to the free-carrier M phase. Our investigation indicates that photoexcitation is an effective method for inducing the I–M transition and elucidates the non-equilibrium physics in bipolaron systems.

Acknowledgments The authors gratefully acknowledge support from the National Natural Science Foundation of China (Grant No. 51705009) and NSAF of China (Grant No. U1530153). H. Y. Liu thanks the Sea Poly Project of Beijing Overseas Talents (SPPBOT).

Fig. 4. Photoexcited phase diagram of TiO$_2$, with constant error bars of ±5 K for visual guidance. $T_{c1}$ and $T_{c2}$ are the LI–HI and HI–M phase-transition temperatures. The colored areas are obtained by polynomial curve fits of $T_{c1}$ and $T_{c2}$.

1) N. F. Mott, Rev. Mod. Phys. 40, 677 (1968).
2) N. F. Mott, Contemp. Phys. 14, 401 (1973).
3) J. Shamblin, M. Heres, H. Zhou, J. Sangoro, M. Lang, J. Neugebauer, J. A. Alonso, and S. Johnston, Nat. Commun. 9, 86 (2018).
4) H. Chu, L. Zhao, A. de la Torre, T. Hogan, S. D. Wilson, and D. Hsieh, Nat. Mater. 16, 200 (2017).
5) P. W. Anderson, Phys. Rev. 109, 1492 (1958).
6) T. Ying, Y. Gu, X. Chen, X. Wang, S. Jin, L. Zhao, W. Zhang, and X. Chen, Sci. Adv. 2, e1501283 (2016).
7) Y. Tokura, M. Kawasaki, and N. Nagaosa, Nat. Phys. 13, 1056 (2017).
8) A. Cavalleri, Cs. Tóth, C. W. Siders, J. A. Squier, F. Ráksi, P. Forget, and J. C. Kielfer, Phys. Rev. Lett. 87, 237401 (2001).
9) X. C. Nie, H.-Y. Song, X. Zhang, P. Gu, S.-B. Liu, F. Li, J.-Q. Meng, Y.-X. Duan, and H. Y. Liu, New J. Phys. 20, 033015 (2018).
10) A. Tomeljak, H. Schafer, D. Stadler, M. Beyer, K. Biljakovic, and J. Demsar, Phys. Rev. Lett. 102, 066404 (2009).
11) J. C. Petersen, S. Kaiser, N. Dean, A. Simoncig, H. Y. Liu, A. L. Cavalieri, C. Cacho, I. C. Turcu, E. Springate, and F. Frassetto, Phys. Rev. Lett. 107, 177402 (2011).
12) H. Y. Liu, I. Gierz, J. C. Petersen, S. Kaiser, A. Simoncig, A. L. Cavalieri, C. Cacho, I. C. Turcu, E. Springate, and F. Frassetto, Phys. Rev. B 88, 045104 (2013).
13) D. Polli, M. Rini, S. Wall, R. W. Schoenlein, Y. Tomioka, Y. Tokura, G. Cerullo, and A. Cavalleri, Nat. Mater. 6, 643 (2007).
14) E. Baldini, T. Kubacka, B. P. P. Mallett, C. Ma, S. M. Koohpayeh, Y. Zhu, C. Bernhard, S. L. Johnson, and F. Carbone, Phys. Rev. B 97, 125149 (2018).
15) C. Schlenker, S. Lakkis, J. M. Coey, and M. Marezio, Phys. Rev. Lett. 32, 1318 (1974).
16) S. Lakkis, C. Schlenker, B. Chakraverty, R. Buder, and M. Marezio, Phys. Rev. B 14, 1429 (1976).
17) M. Watanabe, W. Ueno, and T. Hayashi, J. Lumin. 122–123, 393 (2007).
18) M. Taguchi, A. Chainani, M. Matsunami, R. Eguchi, Y. Takata, M. Yabashi, K. Tamaksa, Y. Nishino, T. Ishikawa, S. Tsuda, S. Watanabe, C.-T. Chen, Y. Senba, H. Ohashi, K. Fujiiwara, Y. Nakamura, H. Takagi, and S. Shin, Phys. Rev. Lett. 104, 106401 (2010).
19) C. Schlenker and M. Marezio, Philos. Mag. B 42, 453 (1980).
20) B. K. Chakraverty, Philos. Mag. B 42, 473 (1980).
21) M. Watanabe and W. Ueno, Phys. Status Solidi C 3, 3456 (2006).
22) H. Kamioka, H. Tsuchida, R. Yamaguchi, T. Tateno, Y. Suzuki, and Y. Fukushima, J. Photochem. Photobiol. A 311, 154 (2015).
23) H. Kamioka, T. Nishitani, H. Tsuchida, R. Yamaguchi, and T. Sueno, Appl. Phys. Lett. 108, 071908 (2016).
24) K. Kobayashi, T. Susaki, A. Fujimoto, T. Tonogai, and H. Takag, Europhys. Lett. 59, 868 (2002).
25) X. Zhong, I. Rungger, P. Zapol, and O. Heinonen, Phys. Rev. B 91, 115143 (2015).
26) M. Weissmann and R. Weht, Phys. Rev. B 84, 144419 (2011).
27) L. Liborio, G. Mallia, and N. Harrison, Phys. Rev. B 79, 245133 (2009).
28) S. Lee, G.-H. Lee, J.-C. Kim, and D.-W. Kim, ACS Catal. 8, 2601 (2018).
29) C. Yao, F. Li, X. Li, and D. Xia, J. Mater. Chem. 22, 16560 (2012).
30) D.-S. Ko, S.-J. Kim, T.-Y. Ahn, S.-D. Kim, Y.-H. Oh, and Y.-W. Kim, Appl. Phys. Lett. 101, 053502 (2012).
31) D.-H. Kwon, K. M. Kim, J. H. Jung, J. M. Jeon, M. H. Lee, G. H. Kim, X.-S. Li, G.-S. Park, B. Lee, S. Han, M. Kim, and C. S. Hwang, Nanotechnol. 14, 5 (2010).
32) D. H. Torchinsky, G. F. Chen, J. L. Luo, N. L. Wang, and N. Gedik, Phys. Rev. Lett. 105, 027005 (2010).
33) Y. C. Tian, W. H. Zhang, F. S. Li, Y. L. Wu, Q. Wu, F. Sun, G. Y. Zhou, L. Wang, X. Ma, Q.-K. Xue, and J. Zhao, Phys. Rev. Lett. 116, 107001 (2016).
34) I. M. Vishik, F. Mahmood, Z. Alpichshev, N. Gedik, J. Higgins, and R. L. Greene, Phys. Rev. B 95, 115125 (2017).
35) D. H. Torchinsky, F. Mahmood, A. T. Bollinger, I. Božović, and N. Gedik, Nat. Mater. 12, 387 (2013).
36) X. C. Nie, H. Y. Song, X. Zhang, S.-B. Liu, Y. Wang, Q. Gao, L. Zhao, X. J. Zhou, J.-Q. Meng, Y.-X. Duan, and H. Y. Liu, arXiv:1803.10506.
37) F. Cilento, C. Giannetti, G. Ferrari, S. Dal Conte, T. Sala, G. Coslovich, M. Rini, A. Cavalleri, and F. Parmigiani, Appl. Phys. Lett. 96, 021102 (2010).
38) L. D. Landau, Z. Phys. 20, 154 (1936).
39) H. Frohlich, H. Pelzer, and S. Zienau, Philos. Mag. 41, 221 (1950).