Carrier Multiplication in Monolayer Transition Metal Dichalcogenides

First-principle calculations of ultrafast charge transfer in Graphene/TMDCs heterostructures

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In Short

- With real-time time-dependent density functional theory method, investigate the carrier multiplication characteristic in monolayer TMDCs.
- Electron-phonon couplings induced narrower bandgap lower the CM threshold energy beyond limit.

Carrier multiplication (CM) is a process whereby absorption of a single photon creates multiple electron-hole pairs. Recently, remarkably efficient CM is observed in layered $MoTe_2$, in which the threshold energy is as low as $2E_g$ with carrier generation QY=2[1,2]. real-time time-dependent density functional theory (rt-TDDFT) method, we investigate CM phenomenon in six monolayer TMDCs MX_2 (M = Mo, W; X = S, Se, Te). For the case of monolayer $MoTe_2$, electron-hole pairs are created with energy of $2E_g$, where the hole and electron excess energy (ΔE_h and ΔE_e) equal to $0.86E_g$ and $0.14E_g$, respectively. In principle, ΔE_h ($0.86E_g$) and ΔE_e ($0.14E_g$) are insufficient to excite another electron from valence bands across the bandgap. Surprisingly, Figure 1 (a) shows that the amount of carriers keeps increasing upon photo excitation and carrier generation quantum yield reaches $\sim$1.07 at 500fs. To reveal the mechanism of CM in monolayer $MoTe_2$, time-evolution of bandgap is plotted in Figure 1(c). Upon excitation, the bandgap of $MoTe_2$ oscillate periodically owing to the nuclear vibrations. Overall, the bandgap becomes narrower along the whole trajectory and even drops to 60% of its initial value, which enables excited holes have sufficient energy to excite additional electron-hole pair across the bandgap. Obviously, the inset of Figure 1(c) shows that $\Delta E_e(t)$ surpasses the bandgap at $\sim$50 fs, triggering CM. In other words, besides energy dissipation, nuclear vibrations can also cause significant changes in electronic structures and carrier relaxation dynamics. To further investigate the influence of phonons on the bandgap, FTs of E_g(t) is plotted in the inset of Figure 1(c). FTs displays a characteristic frequency at $\sim$163.7 cm^{-1} which is associated to the out-of-plane vibrational mode of tellurium atoms (A'). Therefore, it is expected that A'-mode of $MoTe_2$ has impressive effect on the bandgap. Thus, the resulting bandgap reduction favors CM process, especially when the excess energy of carriers $\Delta E_{e/h}$ is below the threshold limit.

We further study the scenario where $MoTe_2$ is excited at different temperatures to identify the positive effect of EPC on CM process (Figure 1). Electron-hole pairs with energy of $2E_g$ are created at 77 K, 300 K and 500 K, respectively. Here, we take account for two type of excitation: (i) asymmetric electron-hole pairs with ΔE_e=$0.14E_g$/ΔE_h=$0.86E_g$ and (ii) symmetric electron-hole pairs with ΔE_e=ΔE_h=$0.50E_g$. To facilitate our analysis, we quantify the CM conversion efficiency as follows $\eta_{CM} = \frac{\phi_{max}-1}{\frac{h\nu}{E_g}-1} \times 100\%$, where ϕ_{max} is the maximum QY in the time evolution process, and $h\nu$ is the energy of phonons. Generally, it is anticipated that weakening EPC is a straightforward method to enhance η_{CM}. However, this viewpoint ignores the influence of nuclear motions. As shown in Figure 1(A), with phonon-induced narrow bandgap, CM phenomenon is observed even when the excess energy ΔE_h is only $0.86E_g$. With a higher temperature, the vibration excursions of atoms are larger. Consequently, a higher carrier generation QY in $MoTe_2$ is achieved via a narrower bandgap. The CM conversion efficiency η_{CM} is promoted from 5.26% to 9.37% when then temperature rising from 77 K to 500 K. Similarly, increasing temperature has the same effect on improving η_{CM} for the symmetric electron-hole pair excitation, as shown in Figure 1(B). Especially, at 77 K and 300 K, CM is not observed, and nonradiative recombination and Auger recombination dominate the carrier relaxation process. This can be explained by the fact that ΔE_h(t) and ΔE_e(t) are both below E_g(t) along the whole trajectory (Figure 1(D)). As discussed above, the oscillation of E_g(t) is caused by A'-mode. However, at 77 K, only a few phonons are excited and E_g(t) keeps much larger than the excess energy of carriers. In contrast, at 500 K, intensive vibrations shrink the bandgap by $\sim$50% and trigger the onset of CM. In this way, we present the possibility to reduce the threshold energy for CM in monolayer TMDCs.

To examine the above mechanism, we excite $MoTe_2$ with energy of $1.75E_g$ at 300K. Precisely, ΔE_e and ΔE_h are $0.58E_g$ and $0.17E_g$, respectively. As shown in Figure 2, CM is indeed observed after excitation, and CM conversion efficiency η_{CM} is $\sim$4% at 500 fs. Figure 2(B) shows that phonon-induced reduction of bandgap is about $0.45E_g$, thus excited electrons have sufficient energy to scatter extra electrons across bandgap at $\sim$150 fs, resulting

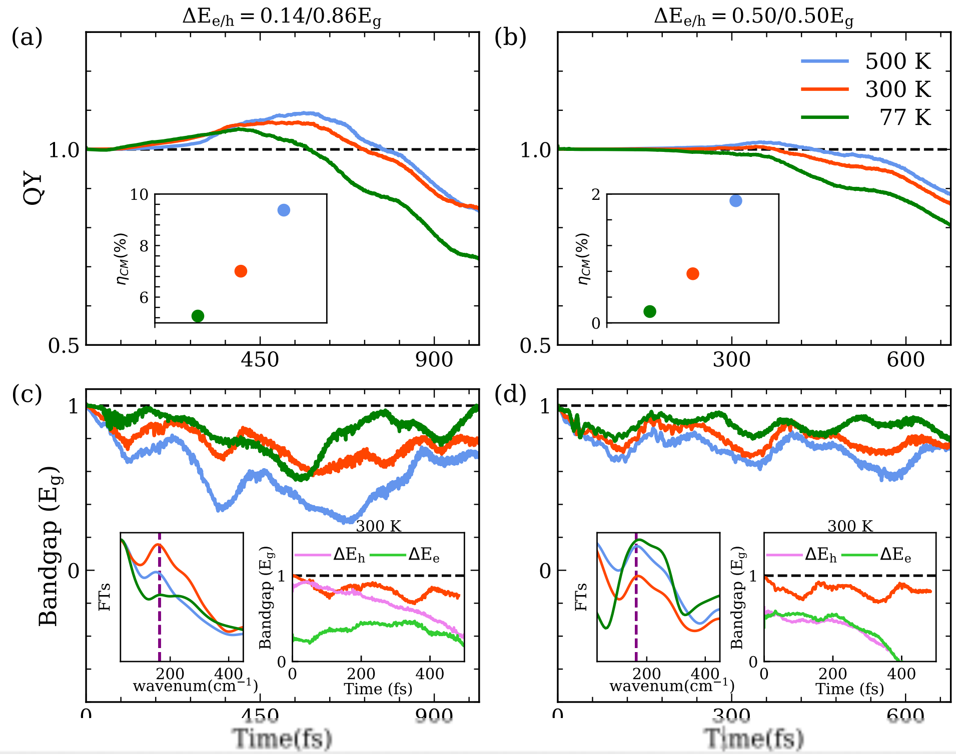

Figure 1: *Excitation dynamics of monolayer $MoTe_2$ with different carrier excess energies at different temperatures. Electron-hole pairs are generated by photon with energy of $2E_g$ at temperature 77 K, 300 K and 500 K. The excess energies of carrier are $\Delta E_{e/h} = 0.14/0.86E_g$ (left panel) and $\Delta E_{e/h} = 0.5E_g/0.5E_g$ (right panel). (A)-(B) Carrier generation QY of CM in $MoTe_2$ as a function of time upon excitation. Inset: CM conversion efficiency at the three temperatures. (C)-(D) $E_g(t)$ 77 K, 300 K and 500 K. Inset: $E_g(t)$ at 300 K is compared with the excess energy of hole ΔE_h and electron ΔE_e, and the dashed line represents the bandgap at $t = 0$ fs. Inset: FTs of time-dependent bandgap $E_g(t)$. Vertical dashed line represents phonon mode A' with vibrational frequency of 163.7 cm^{-1}*

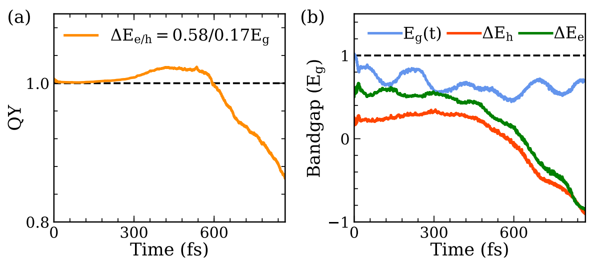

Figure 2: *Excitation dynamics of monolayer $MoTe_2$ with excitation energy of $1.75E_g$. The hole and electron excess energies are $\Delta E_{e/h}$=0.58/0.17E_g. (A) Carrier generation QY as a function of time. (B) Time-evolution of bandgap $E_g(t)$, hole excess energy $\Delta E_h(t)$ and electron excess energy $\Delta E_e(t)$.*

in CM. It is the first time that CM process occurs with excitation energy lower than $2E_g$, which implies that phonons have positive effect on CM process in monolayer TMDCs.

In summary, CM phenomenon can be observedin monolayer TMDCs. Specially, phonon-induced narrower bandgap lower the CM threshold beyond limit.

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https://www.uni-bremen.de/bccms

More Information

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Project Partners

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