Carrier Multiplication in Transition Metal Dichalcogenides Beyond Limit

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

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In Short

- TDDFT calculations and TR-ARPES measurements both demonstrate that the more strongly n-doped graphenethe more efficient CM quantum yield.

The vital goal in the field of optoelectronics is to explore materials which could convert light energy into electrical energy with high efficiency. Materials with CM characteristic, which generate multiple excitons via absorbing one photon, are prospective candidates for optoelectronic devices. Graphene has been considered as a potential photovoltaic material due to its unique electronic and optical properties, including high room-temperature carrier mobility and CM characteristic. CM performance is predicted to be particularly effective in graphene thanks to its linear band structure[1,2], combined with slow electron-phonon cooling[3,4] and strong electron-electron interaction[5,6]. In the past few years, extensive theoretical and experimental efforts have been made to investigate the CM phenomenon in graphene[7–9]. It is reported that CM conversion efficiency is highly sensitive to the location of Fermi level relative to the Dirac point via ultrafast cascade of impact excitation processes[10,11]. Intriguingly, this observation indicates that doping levels can be used to manipulate CM characteristic in graphene, which can be easily tuned by gate voltages[12,13] or intercalating different elements[14,15]. However, the effect of doping level on CM in graphene is still under debate. On the one hand, impact excitation as scattering process result in a chain like cascade consisting of sequential steps with relatively small energy loss per step $\Delta\epsilon \sim E_F$, which indicates that carrier excess energies play a major role in CM conversion efficiency[10]. On the other hand, CM process is directly determined by the probability of excited carriers finding scattering partners in the Fermi sea. In other words, the larger phase space, the more efficient CM[9]. Therefore, we investigate the effect of doping levels on CM in graphene based on NAMD with rt-TDDFT method.

To investigate the effect of doping levels on CM in graphene, two, four, and six carbon atoms are replaced by nitrogen atoms in $6\sqrt{3}\times6\sqrt{3}$ graphene supercell.Nitrogen atoms introduce extra electrons

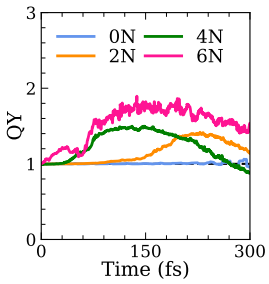

***Figure 1:** CM QY of graphene with different doping levels. The electron-hole pair is generated by phonon with energy of 3.52 eV at 300K.*

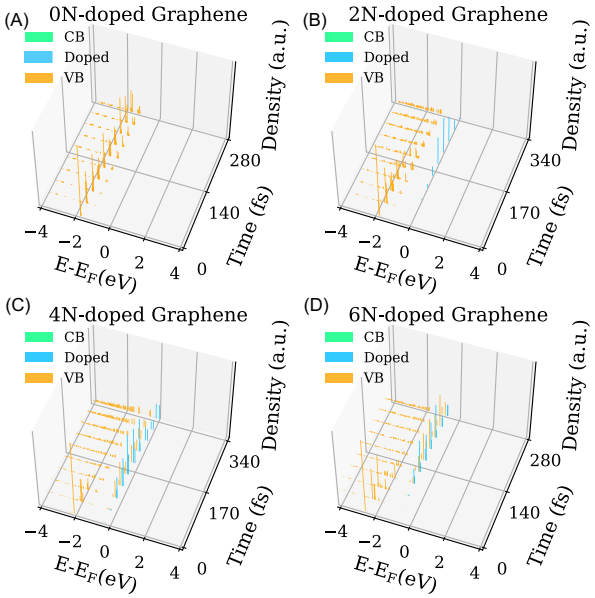

***Figure 2:** Density of excited hole as a function of time and energy. Conduction bands (CB), valence bands (VB), doped states (Doped) are in green, orange and blue, respectively.*

to the system, lifting the Fermi level away from Dirac point by 0.40 eV, 0.58 eV and 0.78 eV respectively. To stimulate the excited carrier relaxation dynamics, a pair of electron-hole is created by moving electron from valence bands to conduction bands at 300 K, with excitation energy of 3.52 eV. In the case of pristine (undoped) graphene, the linear bandstructure leads to a symmetry excitation, in which the electron and hole excess energy (ΔE_e and ΔE_h) both equal to 1.76 eV. Here, the excess energy is defined as the energy difference between excited carriers and Fermi level. In the case of N-doped graphene, due to the change of Fermi level location, the electron

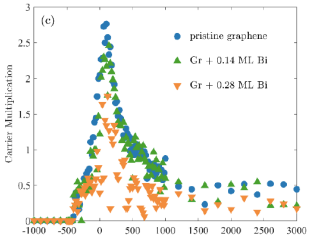

Figure 3: *CM QY after pump and probe pulse in pristine graphene (E_f=0.38 eV), graphene/0.14Bi (E_f=0.38 eV) and graphene/0.28Bi (E_f=0.30 eV).*

excess energies are 1.36 eV, 1.18 eV and 0.98 eV in 2N-doped, 4N-doped and 6N-doped graphene, respectively. To demonstrate the effect of doping levels on CM, we simulate the CM QY in different N-doped graphene. As shown in Figure 1, strongly n-doped graphene indeed triggers more efficient CM. Specifically, the CM QY is increased from 1.41 to 1.89 when the Fermi level is lifted from 0.40 eV to 0.78 eV.

To explore the origin of more efficient CM in strongly doped graphene, we present the density of excited hole as a function of time and energy in undoped, 2N-doped, 4N-doped and 6N-doped graphene. As shown in Figure 2excited holeoccupies higher energy regions, which indicate the occurrence of Auger recombination. Meanwhile, portion of excited holealso distributes in lower energy region, which is related to CM process or phonon-assisted cooling relaxation.Obviously, a portion of excited hole occupies the doped states, especially, the more strongly n-doped graphene, the more excited hole on doped states. In strongly n-doped graphene, photoexcited electron can easily find scattering partner in the Fermi sea to involve in CM process owing to the larger scattering phase space. Thus, CM process prevails over the Auger recombination, dominating the carrier relaxation dynamics.

Consistently, experimental measurements via TR-ARPES also observe the same correlation between doping levels and CM conversion efficiency. It is found that CM QY can be promoted from 1.70 to 2.80 when the Fermi level increasing from 0.30 eV to 0.38 eV (). It is further demonstrated that CM QY mainly depends on available phase space, strongly n-doped graphene provides a larger phase space which boosters electron-electron scattering to enhance CM conversion efficiency. These results provide a practical strategy to promote CM performance in graphene via doping levels, achieving high light energy to electrical energy conversion efficiency in optoelectronic devices.

More Information

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Project Partners

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