Excited state molecular dynamics to study the charge transfer dynamics using TDDFT/B in the frequency and time domain

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

***Prof. Thomas Frauenheim, Yuxiang Liu**, Bremen Center for Computational Materials Science, University of Bremen*

In Short

- With rt-TDDFT/TDDFTB method investigate interlayer ultrafast charge transfer in 2D heterostructure
- The role of orbital coherence in Graphene/TMDCs's heterointerfaces charge dynamics
- External electric field manipulate charge transfer direction and speed after excitation
- Phonon-assisted ultrafast charge transfer at Graphene/TMDCs's heterointerfaces

This project fundamentally aims to study interface charge dynamics in graphene/transition metal dichalcogenides(TMDCs) heterostructures, In the past few years, graphene/TMDCs heterostructures have been considered as prospective exciting material system in electronic and optoelectronics applications due to their efficient interfacial carrier generation. Since graphene is a versatile component to couple with TMDCs due to its high carrier mobility in combination with chemical inertness, high thermal conductance, and extraordinary stability, while TMDCs' wide range of band gap broadens the detection range. Recently, femtosecond time-resolved interfacial carrier transfer study in which photoluminescence coupled with time-resolved pump-probe spectroscopy have successfully capture the carrier dynamics on ultrafast timescale at graphene/TMDCs interfaces[1]. However, the mechanism of the ultrafast charge transfer in graphene/TMDs still remain elusive.

Project objectives The main objective of this project is a detailed comprehension of 2D graphene/TMDCs heterointerface charge dynamics. The aim is to study the mechanism of the interface charge dynamics and investigate practical method to manipulate the charge transfer process. In order to do this, real-time time-dependent density functional theory (rt-TDDFT) coupled with Ehrenfest molecular dynamics will be applied in which the electronic motions are captured by rt-TDDFT and the nuclear evolutions are along with classical molecular dynamics(MD) trajectories.

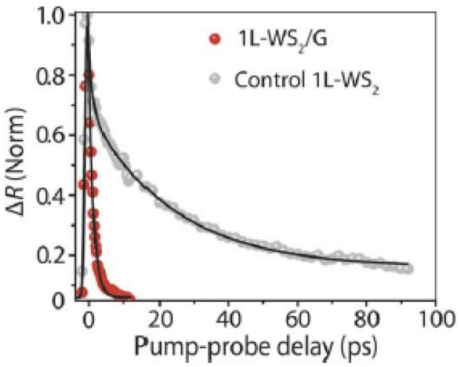

***Figure 1:** Normalized transient dynamics of the one layer Graphene/WS_2 heterostructure at area 3 as marked, and a control 1L-WS2 layer. Solid lines are the fitting curves with exponential decays convoluted with the experimental response function.[1]*

The role of orbital coherence in the charge dynamics at Graphene/WS_2 heterointerface

Recently, many experimental efforts so far have been made to capture the photo-induced ultrafast charge transfer phenomenon in graphene/WS2 heterostructures with time-resolved pump-probe spectroscopy. It shows photo-induced electrons could transfer from WS_2 layer to graphene layer within nearly 1ps, while hole transfer to graphene is on much shorter time of less than 100fs, which is limited by the resolution of experiment equipment[1-3]. [Fig. 1]. The reason for relatively faster hole transfer is still elusive. Our preparatory work shows orbital coherence between donor and acceptor states play a major role in charge dynamics process [Fig. 2], which could provide a new way to manipulate charge transfer for graphene/TMDCs heterostructure used as optoelectronic devices.

To convince the importance of orbital coherence, we will study the layer number effect on the charge transfer process. Monolayer TMDCs are direct band gap semiconductors, while multilayer TMDCs shows indirect band gap characteristics. It seems increasing TMDCs layers will impede the charge dynamics process in the interface region. On the other side, more TMDCs donor states should provide more excited charge transferring to graphene layer. Similarly, multilayer graphene results in the increase of acceptor states, but more layer, longer real-space need to be travel for excited charge states. Two statements seem reasonable. Therefore, it is necessary to investigate the relationship between layer number and orbital coherence which has a profound meaning

for 2D heterostructure application as optoelectronic devices.

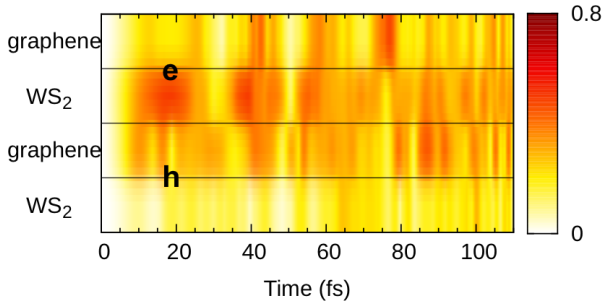

Figure 2: *The evolution of absolutely values of orbital coherence between excited hole (electron) states and neighboring graphene and WS_2 states. The upper two panels represent electron (e) orbital coherence, and lower two panels are hole (h) orbital coherence*

The external electric filed effect on graphene/WS_2 heterointerface charge transfer process

In the past years, some groups concentrated on the electric field tunable interlayer carrier relaxation process in which electric field could manipulate the carrier populations of counterparts, band alignment at heterointerface, and even interlayer coupling, resulting the significant influence on the interlayer carrier relaxation process [4]-[6]. Therefore, vertical external electric filed [Fig. 3] with different values and different directions will be applied to the graphene/WS_2 heterostructure to investigate the electric field effect on interlayer charge transfer, achieving controlling the charge transfer direction and speed.

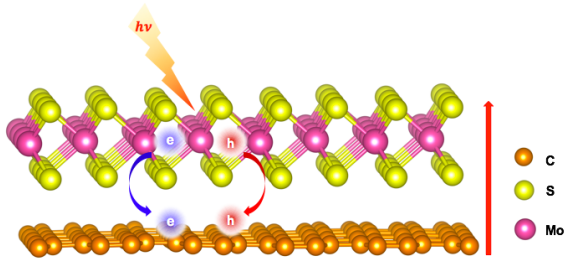

Figure 3: *Illustration of the Graphene/WS_2 heterostructure, where WS2 lies on the top of graphene. Electron and hole carriers excited by incident light transfer from WS2 layer to graphene, the red arrow represents external electric field*

Phonon-assisted ultrafast charge transfer at Graphene/TMDCs's heterointerfaces

With rt-TDDFTB method, the computational complexity will be decreased significantly. Thus, we plan to stimulate a longer time evolution process of graphene/WS_2 layer after excitation. Since with rt-TDDFT method, due to the limitation of computation cost, we only calculate nearly 120 fs dynamics process. According to our preparatory work, we observed some oscillations, hole orbital filling and emptying in graphene states with a dampen amplitude, finally partially localized on graphene layer. We deduce the oscillation is related to graphene and WS_2 vibration mode. However, 120 fs evolution could not capture some of important vibration mode of WS_2, such as $\sim$ 351 cm^{-1} oscillation period 2LA mode and $\sim$ 356 cm^{-1} oscillation period E^1_{2g} mode. Therefore, with rt-TDDFTB method we will investigate the relationship between vibrational mode and charge transfer in graphene/WS_2 heterostructure.

WWW

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

More Information

[1] L. Yuan and T.F. Chung,*et al. Sci. Adv* **4**, e1700324 (2018).

[2] J. He, N. Kumar *et al.*, *Nat. comm.* **5**, 1-5 (2014).

[3] J. He, D. He, *et al.*, *Opt. Express* **8**, 1949-1957 (2017).

[4] Y. L, J. K. Qin, *et al.*, *Adv. Funct. Mater* **26**, 4319-4328 (2016).

[5] M. Massicotte, P. Schmidt, *et al. Nat. Nanotechnol.* **11**,42-46 (2016).

[6] W.J. Yu, Y. Liu, *et al.*, *Nat. Nanotechnol.* **8**, 952-958 (2013).