Atlas of Science
another view on science
https://atlasofscience.org

Layer-dependent fast electron transfer at the Zn-phthalocyanine-few-layer graphene interface: theory explains

The photo-induced effective interfacial charge separation in Zn phthalocyanine/few-layer graphene heterojunctions has been a promising observation for fabrication of efficient energy-conversion devices. Few-layer graphene are two-dimensional (2D) systems composed of one-atom-thick honeycomb layers of sp^2 -hybridized carbon atoms. These materials are proved to be a good charge carrier, have very large mechanical strength and large surface area. In Addition, Zn phthalocyanine (ZnPc), a semiconducting metal complex of phthalocyanine, is a promising photosensitizer that can be used in photo-voltaic and photo-electrochemical applications since it is both thermally and chemically stable compound as well as it has a suitable energy band gap which can be well tuned using appropriate chemical elements.

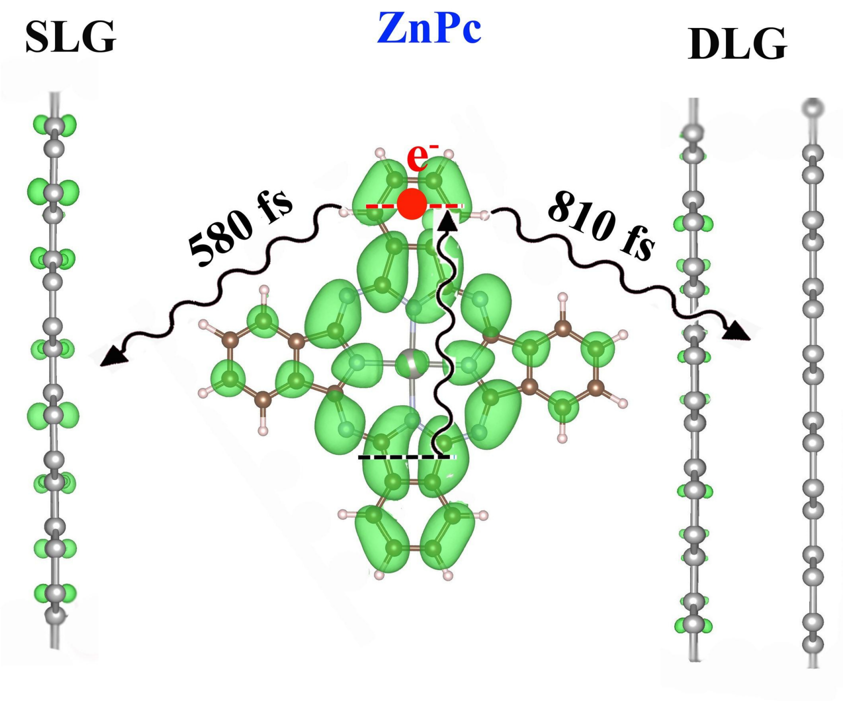

Fig. 1.

Recent time-resolved transient absorption studies demonstrated that the rate of photoinduced interfacial charge transfer from the Zn-phthalocyanine to single-layer graphene (SLG) is faster than to double-layer graphene (DLG), in contrast to the expectation from Fermi's golden rule. For the first time, using time-domain non-adiabatic molecular dynamics (NA-MD) method, we study the electron injection process from photoexcited ZnPc into SLG and DLG substrates. Our calculations suggest that electron transfer (ET) occurs faster in the ZnPc/SLG system than in the ZnPc/DLG system, with 580 fs and 810 fs being the fastest components of the observed electron transfer timescales, respectively. The computed timescales are in close agreement with those reported in the experiment. The computed ET timescales are determined largely by the magnitudes of the non-adiabatic couplings (NAC), which we find to be 4 meV and 2 meV, for the ZnPc/SLG and ZnPc/DLG systems, respectively. The transitions are driven mainly by the ZnPc out-of-plane bending mode at 1100 cm^{-1} and an overtone of fundamental modes in graphene at 2450 cm^{-1}. We find that dephasing occurs on the timescale of 20 fs for both systems, thus a comparable deceleration is observed between the systems when decoherence effects are included. Therefore, we conclude that quantum mechanical decoherence does not notably change the qualitative trends in the ET time scales. We highlight the importance of proper energy level alignment for capturing the qualitative trends in the ET dynamics observed in experiment. Such alignment of energy level rules out any claim that a static DFT or even time-dependent DFT study can explain such counter-intuitive ET trend observed in the measurements. In addition, we illustrate several methodological points that are important for accurately modeling nonadiabatic dynamics in the ZnPc/FLG systems, such as the choice of surface hopping methodology, the use of phase corrections, NAC scaling, and the inclusion of Hubbard terms in the density functional and molecular dynamics calculations.

We believe that our time-domain non-adiabatic molecular dynamic study can well qualitatively explain the counter-intuitive trend in speed of the ET at the interface of the ZnPc and few-layer graphene. In addition, we point out the fact that there is a certain intrinsic limit in using simple static DFT to explain many time-dependent phenomena and be very cautious not use it to study some phenomena although it could give seemingly good interpretation in the first place.

Hamid Mehdipour, Alireza Z. Moshfegh
Department of Physics, Sharif University of Technology, Tehran, Iran

Publication

Dependence of electron transfer dynamics on the number of graphene layers in π-stacked 2D materials: insights from ab initio nonadiabatic molecular dynamics
Hamid Mehdipour, Brendan A Smith, Ali T Rezakhani, Saeedeh S Tafreshi, Nora H de Leeuw, Oleg V Prezhdo, Alireza Z Moshfegh, Alexey V Akimov
Phys Chem Chem Phys. 2019 Oct 24