

Charge separation dynamics at thin-film hetero-junctions using time-resolved terahertz spectroscopy

Andreas F. Bartelt*, Christian Strothkämper, Klaus Schwarzburg, Rainer Eichberger

Helmholtz Center Berlin for Materials and Energy, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany

Andreas.Bartelt@helmholtz-berlin.de

In this contribution, charge separation processes are investigated in different nano-scopic thin-film photovoltaic materials. We will start with the well-known organic donor-acceptor system ZnPc:C₆₀. After excitation with an 800 nm laser pulse, the photo-generated ZnPc-excitons are split at the interface with C₆₀. Taking advantage of the excess energy, some free charges are generated “immediately” (within 1 ps), while others stay Coulombically attracted and form an interfacial charge transfer (CT) state. By increasing the substrate temperature during deposition, the morphology of the blend can be tuned to increase both C₆₀ domain size and crystallinity. Using optical-pump terahertz-probe spectroscopy, we find an increased probability of the interfacial CT states to separate into free charges as the C₆₀ morphology is improved in the blend¹. The charge separation processes improve from both hot and relaxed CT states, and can be connected to the higher I_{SC} in the solar cells.

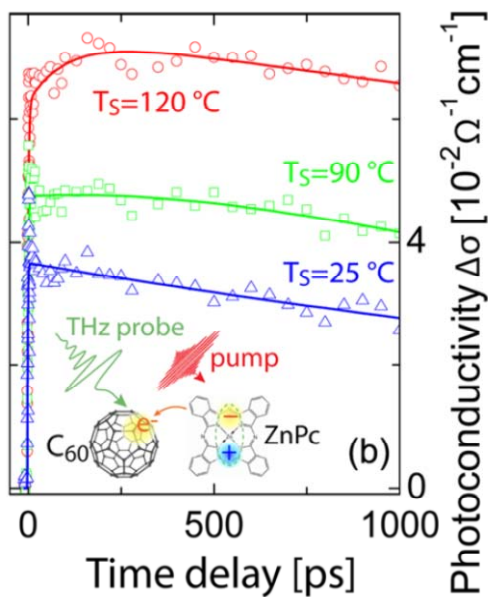
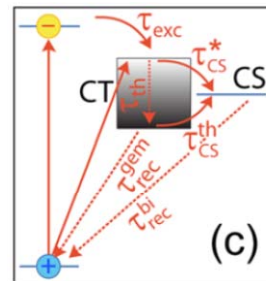


Fig.1: Photoconductivity transients following optical excitation of ZnPc:C₆₀ blend layers grown on substrates with temperatures $T_S=25^\circ\text{C}$, 90°C and 120°C . With increasing T_S , the instantaneous photoconductivity increases while a second and slower rise appears. The signals can be connected to an improved ability to separated hot and relaxed charge-transfer states.



Despite morphological improvements, high driving forces (i.e. large energy differences between donor and acceptor levels) are still needed to separate charges at pure organic interfaces, reducing V_{OC} . One reason is that the charges are poorly screened in the organic materials due to their low dielectric constants of $\epsilon \sim 3$. Using hybrid organic-inorganic materials with higher ϵ inorganic acceptors, separation of charges with smaller driving forces should be feasible due to the lower capture radius. A promising and highly used material in this respect is ZnO with $\epsilon \sim 10$. However, using a combination of optical and

THz transient absorption, significant injection delays from the organic absorber into nanoscopic ZnO acceptors are observed with detrimental effects on charge separation efficiency. We will investigate this phenomenon for different organic dyes varying interfacial structure, chemical environment and temperature.

If the organic absorber is replaced by a thin inorganic layer, an extremely thin absorber solar cell can be constructed. In the third part we will show how charge separation is facilitated when nm thin sulfide layers are coated around ZnO nanorods in a core/shell structure. The charges generated in the ~5-15 nm thin chalcogenide (In_2S_3 , CdSe, CdS) absorber shells by the optical fs laser pulse are observed during passage towards and into the ZnO nanorod cores by the evolution of the photoconductivity detected with the terahertz probe pulses². By comparison with the evolution of the photoconductivity in planar absorber films, clear signatures of charge-separation dynamics are found. By applying a simple trapping-detrapping model, ultrafast carrier capture, release and transport through the absorber layer are simulated, and a slow charge transfer into the ZnO core proceeding over hundreds of picoseconds is found.

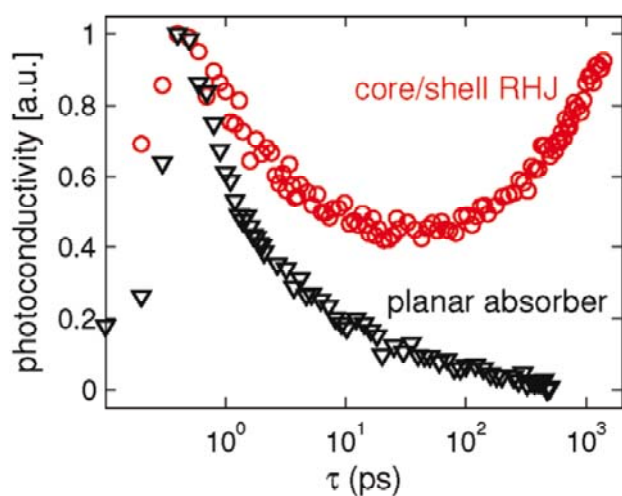


Fig. 2: Comparison of time-dependent photoconductivities for 50 nm thin planar In_2S_3 (black triangles) and $\text{ZnO}/9\text{nm-}\text{In}_2\text{S}_3$ core/shell nanorods (red circles). While the charge carriers immobilize within tens of ps in the planar film, the core/shell structure exhibits the generation of free and highly mobile charges, which are injected from the In_2S_3 absorber into the ZnO core.

¹ A. Bartelt et al., Appl. Phys. Lett. **99**, 143304 (2011).

² C. Strothkaemper et al., J. Phys. Chem C **116**, 1165 (2012)