Excitons in Coupled Nanotube Photovoltaic Thin Films

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We have previously reported on the efficient harvesting of excitons from photoexcited, semiconducting nanotube thin films. The films are interfaced with C_{60} fullerenes to form a type-II heterojunction with band offsets that exceed the exciton binding energy. Excitons photogenerated near the heterointerface are dissociated into separable electrons (which transfer to C_{60}) and holes (which remain on the nanotubes) with quantum efficiency ≈ 90%. This behavior has promise for creating nanotube photoabsorber-based photovoltaic solar cells and photodetectors. However, the efficiency by which excitons can be dissociated remains high only when the nanotube films are thin (5 nm in thickness). The efficiency rapidly decreases as the nanotube film thickness increases, due to poor inter-nanotube exciton migration.

Here, we present on recent work designed to understand and improve exciton migration in coupled nanotube films via theory [1] and experiments [2-4]. We have calculated exciton transfer rates due to Coulomb coupling between nanotubes of varying orientations considering both first- and second-order (phonon-assisted) processes. Second-order dark-to-bright inter-nanotube transfer is as fast as both first and second order bright-to-bright transfer. This important result shows that dark excitonic states are able to efficiently and directly transfer between nanotubes in films.[1] We have tested the hypothesis that poor inter-nanotube exciton migration in films can be attributed to quenching by defects via experiments in which (i) diazonium defects are intentionally added to nanotubes at known concentrations [2] and in which (ii) nanotubes are prepared via three different processes of decreasing harshness: extended ultrasonication, brief ultrasonication, and shear force mixing [3]. Inter-nanotube exciton transfer is then characterized via photoluminescence-, transient absorption-, and device photocurrent spectroscopies. Our results show that poor out-of-plane exciton diffusion depth can be attributed in large part due to losses that arise from the trapping and quenching of excitons by defects induced during processing. Other photovoltaic parameters including fill-factor and open-circuit voltage also improve with decreasing processing harshness.

[1] A.H. Davoody, M.S. Arnold, I. Knezevic et al., *J. Phys. Chem. C*, **121,** 13084−13091 (2017).
[2] J. Wang, J.T. Flach, M.T. Zanni, M.S. Arnold et al., *J. Phys. Chem. C*, **4**, 8310-8318 (2017).
[3] M.J. Shea, J.T. Flach, M.T. Zanni, M.S. Arnold et al., *In Revision* (2018).

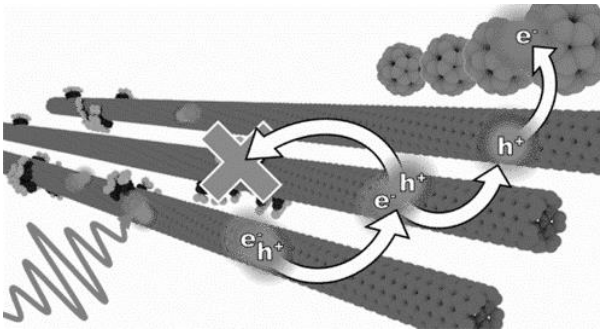

Fig.1. Photogeneration, intra- and inter-nanotube migration, quenching, and dissociation of excitons in coupled nanotube thin films.