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### Electronic Dynamics Underlying Molecular and Nanoplasmonic Light Harvesting

#### Studied by Ultrafast X-Ray Photoelectron Spectroscopy

The success of many emerging molecular electronics and light harvesting concepts hinges on an atomic-scale understanding of the underlying electronic dynamics. Processes evolving on spatial and temporal scales spanning orders of magnitude have to be connected in order to gain a comprehensive picture of the fundamental steps that enable molecular, interfacial, and macroscopic charge and energy transport. The presentation will focus on the potential of ultrafast X-ray photoelectron spectroscopy to provide a deeper understanding of photoinduced electronic dynamics in several model systems for light harvesting by heterogeneous molecular, molecule-semiconductor, and nanoplasmonic architectures.

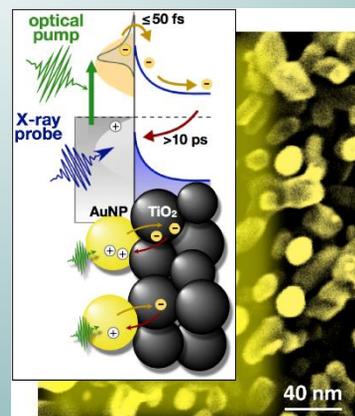
Using femtosecond and picosecond time-resolved X-ray photoelectron spectroscopy (TRXPS) to study photoinduced charge injection in N3 dye-sensitized films of ZnO nanoparticles, the locations of intermittently trapped electrons, interfacial dipoles, as well as charge delocalization and recombination dynamics are monitored with interfacial site-specificity, resolving a long-standing controversy regarding the bottleneck for charge injection in ZnO based dye-sensitized systems.

TRXPS studies of photoinduced dynamics in copper-phthalocyanine(CuPc)-C60 heterojunctions provide a deeper understanding of the predominant energy transport and charge generation mechanisms. Contrary to common belief, fast intersystem crossing from initially excited singlet excitons to triplet excitons within the bulk of the donor domain is not a loss channel but the triplet excitons contribute to a significantly larger extent to the time-integrated interfacial charge than the initially excited interfacial singlet excitons. Ultrafast site-specific X-ray probing provides direct access to the diffusivity of the triplet excitons in the CuPc donor domain and their diffusion length. A recent TRXPS study of the CuPc-C60 heterojunction in the femtosecond domain captures the actual moment of charge generation from interfacial charge-transfer (ICT) states and provides a quantitative measure of the exciton dissociation efficiency compared to photon energy loss by exciton recombination.

In a third showcase example, photoinduced charge transfer dynamics in a nanoporous film of TiO<sub>2</sub> sensitized with gold nanoparticles (Au NPs) is monitored by TRXPS. Direct access to the absolute photon-to-charge conversion efficiency and subsequent electron-hole recombination dynamics in this model system for plasmon-enabled photocatalytic nano-assemblies is demonstrated with single-electron sensitivity. The results provide important boundary conditions for the design of AuNP-TiO<sub>2</sub> based light harvesting systems. Opportunities for extending the measurements toward studies of photoinduced chemical transformations will be discussed.

#### References

- [1] F. Roth et al., Direct Observation of Charge Separation in an Organic Light Harvesting System by Femtosecond Time-Resolved XPS, *Nat. Commun.* 12, 1196 (2021).
- [2] M. Borgwardt et al., Photoinduced Charge Carrier Dynamics and Electron Injection Efficiencies in Au Nanoparticle-Sensitized TiO<sub>2</sub> Determined with Picosecond Time-Resolved X-Ray Photoelectron Spectroscopy, *J. Phys. Chem. Lett.* 11, 5476 (2020).
- [3] F. Roth et al., Efficient Charge Generation from Triplet Excitons in Metal-Organic Heterojunctions, *Phys. Rev. B* 99, 020303(R) (2019).
- [4] O. Gessner and M. Gühr, Monitoring Ultrafast Chemical Dynamics by Time-Domain X-Ray Photo- and Auger-Electron Spectroscopy, *Acc. Chem. Res.* 49, 138 (2016).



**Tuesday, 22.06.2021, at 17:15 h online (link t.b.a.)**

Innsbruck Physics Colloquium, Organisation: M. Beyer, H.-C. Nägerl, A. Reimer