Ultrafast Charge Transfer Dynamics in a Plasmonic Photocatalyst Studied by Femtosecond Time-Resolved X-ray Photoelectron Spectroscopy

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Heterogeneous interfaces between metal nanoparticles (MeNPs) and transition metal semiconductors (SCs) attract significant attention due to their potential to provide routes to renewable, carbon-free energy production and storage through processes such as photocatalytic hydrogen generation from water. A particularly intensely studied model system for photochemical water splitting consists of plasmonically active, spherical gold nanoparticles (AuNPs) attached to nanocrystalline TiO₂ substrates, shown in Figure 1. Despite significant efforts, the overall efficiencies of plasmonic light harvesting systems generally remain rather low, requiring a deeper understanding of the fundamental dynamics underlying their function. Currently, charge transfer (CT) between MeNPs and SCs is commonly described by either plasmon-induced hot-electron transfer (PHET) or plasmon-induced metal-to-semiconductor interfacial charge transfer transitions (PICTT). To gain a deeper understanding of these competing processes, we have measured the ultrafast interfacial charge injection and recombination dynamics for AuNP sensitized TiO₂ at the FLASH Free Electron Laser in Hamburg under UHV and water exposed conditions via femtosecond Time-resolved X-ray Photoelectron Spectroscopy (TRXPS). The results will be discussed within a kinetic model considering various CT and relaxation channels. The model is complemented by high-level ab-initio calculations based on constrained density functional theory.

Keywords: Charge transfer, photocatalysis, nanoplasmonics, FELs, time-resolved XPS.



Figure 1. a) Conceptual representation of competing electronic processes after photoexcitation. **b)** Transient Au4f photoemission spectra during photoinduced CT in the AuNP/TiO₂ system recorded at FLASH.