Excited States at Metal-Semiconductor Interfaces: Carrier Transport and Selective Photo-electrocatalysis

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Harvesting non-equilibrium carriers at semiconductor-metal interfaces offers an opportunity to modify the rates and pathways for photochemical reactions at the nanoscale. The carrier generation, transport and interface dynamics can be addressed with a combination of first-principles theory for carrier excitation and relaxation, observation of carrier dynamics via hot-carrier photocurrent spectroscopy, ultrafast transient absorption spectroscopy, and photoelectrochemical measurements that assess current transport, product yield and selectivity. We use as an example the gold/gallium nitride interface and compare results of theory to excited carrier transport, transient absorption and photocatalysis measurements.

We also report the first known example of photoexcited hot hole injection at a metal-p-type wide bandgap semiconductor interface. Despite the presence of an interfacial Schottky barrier to hot-hole injection of more than 1 eV across the Au/p-GaN heterojunction, plasmonic Au/p-GaN photocathodes exhibit photoelectrochemical properties consistent with the injection of hot holes from Au nanoparticles into p-GaN upon plasmon excitation. The incident photon-electron conversion efficiency spectrum for the plasmonic photocathodes faithfully follows the surface plasmon resonance absorption spectrum of the Au nanoparticles, and a sustained photovoltage during plasmon excitation of plasmon-induced hot-hole capture and conversion, using a gold/p-type gallium nitride (Au/p-GaN) interface conditions tailored for studying photoelectrochemical CO_2 reduction.

Whereas the Au/p-GaN structure has an interfacial Schottky barrier to hot-hole injection of more than 1 eV, the Au/p-NiO has an approximately zero Schottky barrier height.. Taken together, our results offer experimental validation of photoexcited hot holes in high-barrier Au/p-GaN structures and also in low-barrier structures, such as Au/NiO.

These results, together with other recent advances, form an outlook for the use of photoexcited carriers as a tool for altering selectivity in photon-driven catalytic processes.