Unraveling charge and energy transfer dynamics between plasmonic metals and adsorbates

Savini Bandaranayake[1], Paul Schrader[1], Liang Tan[2], Krupa Ramasesha[1]

[1]*Combustion Research Facility, Sandia National Laboratories, Livermore, CA, USA*

[2]*Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA, USA*

Plasmonic metals are potential candidates for photocatalysis due to their tailorable light-matter interactions, which allows absorption of a significant portion of the solar energy spectrum with large cross-sections. The reactants and intermediates are adsorbed onto the plasmonic metal surface, and following the photoexcitation, the charge and/or energy transfer to the adsorbate drives the chemical transformation during photocatalysis. In this presentation, I will discuss our efforts to unravel ultrafast charge and energy transfer mechanisms using a model plasmonic metal-adsorbate photocatalyst: a thin gold film with a self assembled monolayer of 4-mercaptobenzoic acid (MBA). Ultrafast UV-visible transient spectroscopy was utilized to study photo-induced carrier dynamics of gold and MBA-gold upon interband (400 nm) and intraband (800 nm) excitations. The results suggests an elongation of electron-phonon (el-ph) and phonon-phonon (ph-ph) scattering rates when MBA is adsorbed onto gold compared to pristine gold. It is likely that el-ph scattering rate is slowed by hot electron trapping at the delocalized, lowest unoccupied molecular orbital (LUMO) in MBA-Au, mediating carrier recombination and that ph-ph lifetimes are extended due to the steric strain by MBA on Au atoms. Furthermore, ongoing theoretical investigations using real-time time-dependent density functional theory aim to interpret and support these experimental results.

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