The surface plasmon polariton is a coupled phenomenon which mixes together electromagnetic waves and the conduction electrons in a material, resulting in the generation of a single quasi-particle. The surface plasmon polariton is characterized by a strongly amplified electric field and the metal nanoparticles supporting it have a cross section typically much larger than the geometrical one. This makes metal nanoparticles very efficient in terms of harvesting incident light and utilizing the enhanced electric fields to amplify many physical processes, which efficiency depends on the intensity of the electromagnetic field. Once excited, the surface plasmon decays either by radiatively emitting a photon or by absorption. Radiation of plasmons was and still is a useful channel which enables a lot of applications, such as ultra-sensitive single molecule detectors or directional, highly-compact antennas.

On the other hand, the absorptive channel was, for a long time, considered to be an unwanted, parasitic effect which decreases the efficiency of plasmonic devices. This is indeed true in many cases for devices based on far-field observations or plasmon propagation along metal-dielectric interfaces. However, when one realizes that absorption of a plasmon generates energetic charge carriers, these “losses” take on new possibilities. When one is able to harness these so-called hot electrons, or indeed hot holes, from the metal nanoparticle or a nearby acceptor it becomes possible to utilize plasmons toward various means, such as photodetectors, enhanced photovoltaics, photothermal cancer therapy, or plasmon-enhanced catalysis. However, in order to extract these energetic charge carriers from the metal nanoparticles, it is necessary to know how their properties evolve with the nanoscale structuring of the plasmonic particle, its composition, nearby objects such as other plasmonic antennas or the active acceptors – molecules, semiconducting materials. Such physical understanding is present at the scale of tens-of-nanometers, however, is lacking in many aspects at the atomic scale.

In the project we aim at elucidating how at the atomic scale nanoparticles composed of non-noble transition metals respond to optical excitation, how to model the excitation of their plasmons using time-dependent density-functional-theory (TD-DFT), how to use this knowledge and these results to quantify hot carrier generation in such non-noble metal nanoparticles, and how these plasmon-generated hot carriers can be injected into nearby acceptors – molecules or semiconductors. Due to the time-frame available in TD-DFT, we will focus on direct transfer of hot charge carriers from metals to acceptors (also known as chemical interface damping) as well as enhanced intra-acceptor excitation. We will also study how these above enumerated phenomena depend on the internal composition and structure of the nanoparticles by admixing noble metals to increase the efficiency of the plasmon by decreasing its losses, but this modification will need to rationally designed to ensure that “useful” hot carrier generation will not be compromised, but increased.

Realization of the project will enable physical understanding of underlying processes which govern hot electron/hole generation from an excited plasmon in various types of metal nanoparticles. It will allow rational design of multifunctional complexes that can capture, convert, and direct incident photons into useful work. Applications based on such solutions will include more efficient photo-catalysts, ultra-sensitive photodetectors, or highly efficient photovoltaics.