Application of time-resolved X-ray spectroscopy to determine electron and hole energy distributions upon plasmonic excitation of metallic nanoparticles.

In order to face the energy and ecological requests, we need a compelling economic vision for the world based on carbon-neutral and carbon-free energy, including in the production of chemicals. Solar-driven chemistry converting small molecules, such as N_2, H_2O and CO_2, into chemicals and fuels with direct sunlight, also referred to as artificial photosynthesis, provides a direct pathway to wean off our fossil fuel dependence and develop a carbon-neutral economy. Most of the artificial photosynthesis processes involve multi-carriers, and thus there is a relentless pursue to find photosensitizers that accomplish this requirement.

Metal nanoparticles (NPs) based on Au, Ag, Cu, and Al exhibit an intense light absorption and scattering in the region of the solar spectrum due to the excitation of collective electronic excited states (plasmons). At visible wavelengths, the interaction of the incident light with conduction band electrons of NPs resonantly excites coherent oscillations of the electron density of states. This phenomenon is called localized surface plasmon resonance (LSPR) and allows the generated hot electron clouds to be used as triggers for light-induced energy conversion and storage processes. At present, the decay processes of LSPR are recognized and reasonably well understood, including the sequence of scattering and relaxation mechanisms together with effects of the size and shape of NPs. However, a number of unanswered questions remain, despite numerous optical studies on the ultrafast dynamics of plasmonic excitation (Figure 1). The energy distribution of the hot electrons photo-generated from LSPR in NPs and hybrid systems remains unspecified. It is believed that LSPR excitation leads to the formation of hot electrons with an array of energies, and only those with sufficient energy can be transferred to the semiconductor. Therefore, determination of hot electron and holes energy distributions is thus vital as this property translates directly to the system efficiency and determines how efficiently the light absorption in NPs can be employed to drive chemical reactions. To accomplish the project goals, novel methodological approaches will be developed and implemented at newest X-ray facility: X-ray Free Electron Laser. The implementation of the project will have a large impact on research not only in the field of material's physics but also will provide scientists with a new concept and a new methodology to bypass current measurement barriers.

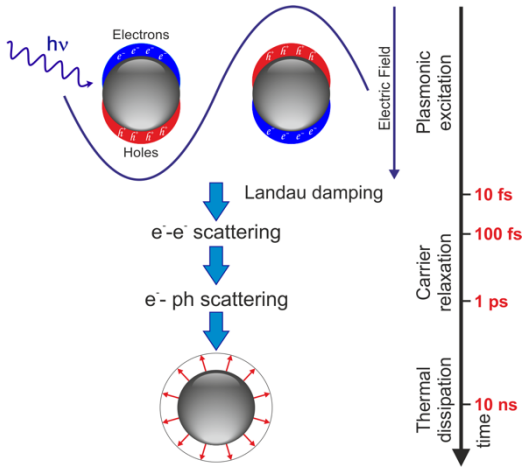

***Figure**: Schematic representation of localised surface plasmon resonance (LSPR) excitation and relaxation processes in a metallic nanoparticle: electron-electron scattering (<100fsec), electron – phonon scattering (<10 psec), phonon-phonon scattering and heat dissipation (<10nsec).*