C1. PROJECT SUMMARY FOR THE GENERAL PUBLIC

One of the major challenges of modern science is to develop scalable low-cost systems capable of converting solar radiation into usable forms of energy, whether electrical or chemical[1,2]. Earth-abundant elements (e.g. Fe, Co, Mn) would be most desired for this purpose, but mostly very scarce elements, like noble metals, i.e. Ru, Ir, Pt, have proven their utility so far. In order to make the transition to cheap devices (with abundant transition metal elements, or radically higher efficiency in the case of scarce elements) contemporary chemical engineering efforts seek to alter the molecular structure in order to achieve efficient function, and the initial properties are characterized with standard electrochemical methods.

The goal of the project is to allow going beyond the current incremental gains in the performance of light conversion devices without a thorough understanding about the detailed reasons for success or failure of selected systems, seeking to establish a new paradigm for improving such systems with the acquired most fundamental knowledge. In order to establish this new paradigm, both the electronic and structural degrees of freedom must be determined on the fundamental timescales of electron transfer process that is on a few tens of femtoseconds (10^{-15} s) to few picoseconds (10^{-12} s) timescale. To view the electrons at work in these systems, we will apply advanced ultrafast (time-resolved) X-ray techniques implemented at the world's most powerful X-ray sources, namely the X-ray Free Electron Lasers (XFEL). XFELs allow monitoring both electronic and structural dynamic processes, and this simultaneously in one single experiment. This new tool has thus the potential to reveal the initial steps leading to the desired photovoltaic or photocatalytical activity. It has also the capability to deliver new information about the reasons for a decreased or enhanced functional efficiency, and not just about the efficiency itself.

The project will develop and employ experimental methodologies at the very frontier of X-ray science by using a combination of time-resolved X-ray absorption spectroscopy and X-ray emission spectroscopy at both synchrotron and XFEL sources. This approach will allow tracking the chemical reactivity and the underlying electronic (charge state, spin state, unoccupied density of states, etc.) and geometrical (interatomic bond distances and angles) changes of short-lived transition states at the same time. The techniques used in this project will provide atomic-scale spatial resolution, element specificity, and the possibility to disentangle interactions with the solvent environment. Recent work has pioneered the implementation of this combination of techniques at established synchrotron and the most modern XFEL sources available[3] to characterize charge transfer mechanisms and structural response to light[4,5].

By implementing these advanced ultrafast X-ray techniques it will become possible to deliver a more complete understanding of elementary molecular processes that govern the chemical reactivity on the very fundamental level. Furthermore this new understanding will be utilized to engineer more efficient transition metal compounds for molecular photosensitization. In this respect, the present project will target two fields of solar energy conversion, namely *photocatalytic*, where it will focus on studies of novel materials that not only are able to utilize solar energy to split water with high efficiency, but also show the extraordinary stability necessary for large-scale device implementation. Moreover, it will also focus on *photovoltaics*, in particular the novel types of photosensitizers that could be used in dye-sensitized solar cells, and the mechanistic implications of the involved electron transfer processes, which could be addressed with the specific set of structure-sensitive ultrafast X-ray probes.

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