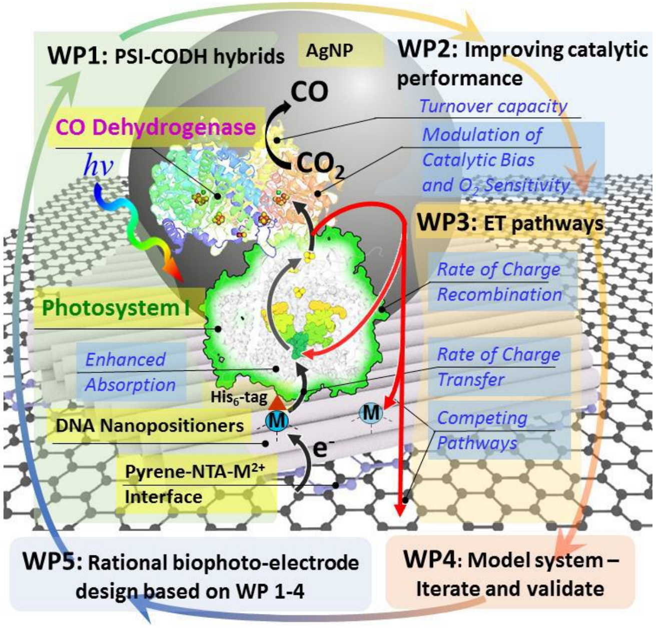
The SUNCOCAT proposal aims at the nanoscale engineering of electron and energy transfer pathways and ultimately, the development of efficient biophotoelectrodes, to capture solar light and convert CO_2 to carbon monoxide, the latter product being an important platform chemical and fuel. This novel class of the hybrid photoelectrodes will employ the strong reducing power of photosystem I (PSI) to drive the high performance of the CO_2 converting biocatalyst, CO dehydrogenase (CODH). A robust extremophilic PSI will serve as the central light harvesting and charge separating biocatalyst, capable of capturing solar energy in the visible part of the solar spectrum to drive reductive chemistry. Photoactivated electrons generated by PSI upon visible light capture will be wired to novel O_2-tolerant CODH variants for conversion of atmospheric CO_2 into CO. The well-structured and oriented attachment of the PSI-CODH hybrids to the electrode surface *via* the DNA building blocks is the breakthrough approach of this proposal for enhanced solar energy capture and conversion into fuel. To achieve the highest possible energy conversion efficiency, SUNCOCAT uses a highly interdisciplinary approach based on both fundamental electrochemical investigation and quantum mechanical/molecular mechanics (QM/MM) modelling of electron transfer together with a number of physico-chemical, genetic, and biophysical methods in order to efficiently interface the abiotic and biotic components for solar-driven reduction of CO_2 to CO, aiming at high product selectivity and yield.



Rational assembly of the robust biophotocatalytic assemblies onto the electrode surface with the use of advanced physico-chemical methods (molecular wiring, DNA origami technique and plasmonic enhancement of absorption and fluorescence), as well as oriented coupling of the hybrids to earth-abundant conductive materials, i.e., single layer graphene on fluorine-doped tin oxide, will be used to optimise the energy and charge transfer within the hybrid photoelectrode for efficient solar-driven chemical conversion.