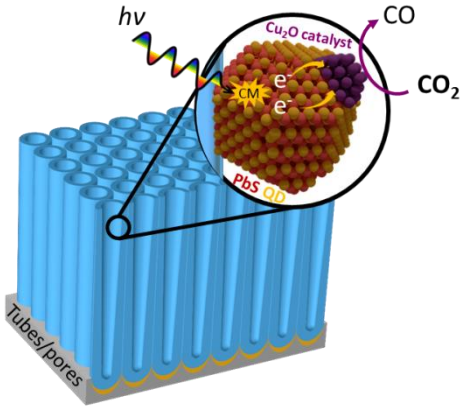
Solar Reduction of CO_2 at Nano-Architectured Photoelectrodes Featuring Advanced Photon Management (SOLAFAME)

Popular Science Summary



The time has come to care for our planet. Drastic man-made environmental changes such as the increase in average temperature, air pollution, and vast amounts of plastic in the oceans significantly lower health safety and biodiversity. Following the disturbing effects and growing awareness of society, both social and legislative solutions have been initiated towards minimizing the devastation. Among the solutions, increased focus must be placed upon utilizing renewable energy and material sources for producing fuels and raw chemicals to achieve the EU goal of a low-carbon economy by 2050. Silicon photovoltaics, hydroelectric, and wind turbines are all mature technologies applied to this grand challenge, but there are limits to their ability to satisfy energy demands. In order to exploit the promise of renewable fuel production, we need to learn how to drive chemical reactions requiring large/concentrated amounts of energy using new, clever designs. Nanomaterials provide several unique properties to approach these challenges. The ability to manipulate both photophysics and catalysis based on geometric design can be put to use to obtain efficient sunlight-driven fuel production *via* water oxidation combined with CO_2 reduction ('artificial photosynthesis').

The intricate processes associated with CO_2 reduction (CO_2red) require further study to make solar fuel production a reality. The present challenges are the multiple-electron reduction mechanism, the competing hydrogen evolution reaction, the low solubility of CO_2 in water, and the inert C=O bond (energy 750 $kJ \cdot mol^{-1}$). The consortium partners consisting of two experienced research groups from FAU and IMP PAN propose a modular approach to designing separately photoelectrodes for CO_2red and H_2O oxidation (H_2Ooxid) and adjusting them to each other in a device based on two light absorbing layers in a 'Z-scheme'. We propose to exploit highly ordered substrates that, under further modification, yield advanced photoelectrodes of a solar driven reactor.

One innovation of the SOLFAME project will consist in exploiting 'carrier multiplication'. This phenomenon consists in the conversion of one highly energetic electron (and its corresponding so-called 'hole') into two electrons, each of lower energy. To reduce CO_2, we plan to use the nanometer-scale properties of quantum dots (QDs) to generate an increased density of electrons using carrier multiplication. This will address the challenge of the multi-electron reaction pathway necessary at the Cu or Cu_2O catalyst to drive CO_2 reduction (CO_2red). In the second innovation of SOLFAME, we will integrate this QD/catalyst material system into an array of nanopores formed from an anodized matrix. This geometry will allow us to increase the available surface area at which the reaction takes place by orders of magnitude. Thus, it will circumvent the issue of low CO_2 concentration in water. On the complementary electrode, the H_2Ooxid step will be performed on anodized TiO_2 nanotubes coated using atomic layer deposition with the light absorber Sb_2S_3 and a catalyst of Ir/V_2O_5. Both electrodes take advantage of not only the deposited materials' properties but also the high ordering of the substrate, which facilitates optimal light capture and charge transport. We will verify the enhanced operational efficiency of the whole system composed of both optimized electrode materials exhibiting complementary light absorption spectra. To increase the photogenerated electrical potential driving the reaction, the photoelectrodes will be combined in a tandem cell.

A pH-neutral environment yields the proper energetics for the described photoelectrodes and provides straightforward advanced control of:

a) The extent of light absorption - by changing the absorber layer thickness and tube or pore dimensions, and
b) The spectrum absorbed - by adjusting the size of QDs or stoichiometry of materials.

By the combination of complex physical and chemical characterization (including time-resolved spectroscopy, in-situ spectroelectrochemical measurements) as well as verification of CO_2 photoconversion efficiency within the lab-scale tandem cell, we will overcome the limitations of state-of-the-art artificial photosynthesis designs.