Design and synthesis of multicomponent metal-organic framework heterostructures for efficient and selective CO_2 photoconversion into valuable fuels and chemicals

Currently, fossil fuels (non-renewable resources) are increasingly used as the main source of energy. Excessive consumption of fossil fuels is accompanied by, among others anthropogenic CO_2 emissions to the atmosphere, which in turn leads to global environmental changes (including global warming). CO_2 can be converted into useful hydrocarbons (such as CH_4, C_2H_6, CH_3OH, C_2H_5OH, HCOOH, CH_3COOH, HCHO) using, among others photocatalytic processes, thermochemical, catalytic conversion and photoelectrochemical processes. However, photocatalytic processes have a huge advantage compared to other methods, namely the driving force of photocatalytic reduction of CO_2 to useful hydrocarbons is only solar energy (desirable mainly in the visible solar spectrum), a free and above all renewable energy source, and the transformation of CO_2 is not accompanied by the generation of harmful by-products. Recently, metal-organic frameworks (MOFs), as hybrid crystalline materials, possessing high specific surface area and controllable pore sizes are potentially attractive materials for CO_2 conversion through chemical fixation and photocatalytic transformation. Despite the use of different MOFs for CO_2 photoconversion, there are still limitations such as low efficiency of photogenerated charge carriers separation and mismatching between abilities to effective light absorption and CO_2 adsorption, and therefore this technology still cannot satisfy the practical needs.

The research proposed in the project is related to: (1) development of a new group of MOF-MOF heterostructure materials with a strictly defined morphology, i.e. core-shell, yolk-shell, core-satellite and asymmetric, where first MOF will perform the role of co-catalyst providing among others highly reactive adsorption sites of CO_2 and thus minimalizing activation energy needed to conduct photoreduction reaction towards useful hydrocarbons *via* direct electron transfer from the second component of hybrid - semiconducting MOF (visible light active); and (2) investigation of a fundamental mechanisms of CO_2 photoconversion occurring in the presence of MOF-MOF heterostructures using in-situ techniques and action spectra analysis.

Obtained heterostructures will be comprehensively characterized using microscopic (SEM, SEM-EDX, HR-TEM, TEM-EDX-EELS), spectroscopic (PL, DRS UV-Vis, FTIR, Raman, XPS) and X-ray (XRD) methods. The specific surface and adsorption capacity (relative to CO_2 and selected hydrocarbons) will be determined by the specific surface and porosity analyzer. The dynamics of charge transfer in MOF-MOF heterostructures will be examined using electrochemical and spectroscopic methods (photocurrent and photopotential measurements as a function of time, impedance measurements of photopotential and photocurrent with modulated light intensity, electrochemical impedance spectroscopy and time-resolved photoluminescence spectroscopy). The obtained materials will be tested in the CO_2 photoconversion reaction under the influence of UV-Vis and Vis irradiation (reactions in the gas phase and in the water phase with saturated CO_2). Finally, for the most promising hybrid materials, the mechanism of CO_2 photoconversion into useful fuels and chemical compounds will be studied using in-situ techniques under conditions of CO_2 photoconversion and action spectral analysis.

The expected achievement of this project will be progress in the research of new materials with improved ability (compared to currently known materials) of CO_2 photoconversion into useful fuels and chemical compounds. On the other hand, the study of CO_2 photoconversion mechanism will allow the formulation of general conclusions about MOF-MOF heterostructures. Knowledge in this area may prove to be crucial in the design of new, inexpensive and non-toxic materials with high efficiency in visible irradiation-induced photocatalytic processes.