

The mimic of nature seems to be very tentative in view of the already exceeded the natural carbon cycle. By photosynthesis, nature shows us potential pathways how to tap solar energy and convert it into usable energy. However, what readily take place in nature, is more difficult to adapt to a large scale production of solar fuels. Moreover, human beings consume the natural sources faster than they can form, hence, the concentration of the greenhouse gas will be a serious problem in the near future. Therefore, development of an effective approach to the artificial conversion of CO<sub>2</sub> becomes urgent and ultimate solution in order to provide forthcoming generations with fuels and clean energy in a sustainable way.

The use of energy which arrives from the Sun to the upper atmosphere of the Earth continuously is of particular global interest because this energy is several orders of magnitudes higher than other renewables sources of energy. Another advantage of the solar energy is that, the sunlight driven conversion of solar to chemical energy allows to store large amounts of energy in chemical bonds than can be released in a carbon neutral cycle or be reused in any carbon based technology. The molecule of CO<sub>2</sub> represents high stability and resists to direct splitting even at high temperature at about 2000°C. Thus, the energy input required to overcome the uphill reduction of CO<sub>2</sub> to hydrocarbons with a highly positive change in Gibbs free energy, might be provided by the incident light. The activation of this very stable molecule initiates multistep sequent reactions leading to formation CO<sub>2</sub><sup>-</sup> species by transferring an electron from excited photocatalyst to the lowest unoccupied molecular orbital (LUMO) of CO<sub>2</sub>. Generation of only this first intermediate, occurs at relatively negative potential of -1.89 V vs SHE. Further steps involve formation of products, determined by the number of electrons and protons taking part in the chemical reaction. However, the particular productions are not well separated by the potential, thus the control between various products must come from careful choice of the catalyst or/and co-catalyst and reduction conditions. Therefore, **it is essential to understand the initial CO<sub>2</sub> absorption and its activation mechanism, in order to promote CO<sub>2</sub> reduction efficiency.** Recognition and understanding of an individual process give already a picture of a whole system. In this regard, the electro-reduction of CO<sub>2</sub> is receiving considerable interest over years in view of possible production of carbon-based energy carriers.

The copper, arguably or not, still remains the only metal able to catalyze the reduction of CO<sub>2</sub> with formation of significant amounts of hydrocarbons at high reaction rates over sustained periods of time. However, the high overvoltage required for this conversion and the performance of the copper electrodes suffering from heavy deactivation are the major drawbacks. Therefore the activation of the catalyst through formation of the resonant surface plasmons might be a key factor determining the long term effectiveness and stability of the working system toward CO<sub>2</sub> reduction.

The significance to investigate reduction of CO<sub>2</sub> at gold, silver and copper surfaces enhanced by the extra activation of the process provided by the illuminated, incorporated plasmonic metallic nanostructures (NS) is supported by the occurrence of the photo-emission process associated with the decay of photo-excited surface plasmons. However, while copper facilitates the reaction of CO towards production of hydrocarbons, aldehydes and alcohols, silver together with gold belongs to this group of metals which bind CO<sub>2</sub> or stabilize the CO<sub>2</sub><sup>-</sup>, thus release the CO as the only product of CO<sub>2</sub> reduction. A solution might be alloying of bimetallic systems consisting of gold or silver with copper or palladium nanoparticles which will affect the binding strength of intermediates on a catalyst surface in order to enhance the reaction kinetics for the CO<sub>2</sub> reduction.

Investigations of the photo-induced phenomena enabling to improve and understand fundamental processes involved in CO<sub>2</sub> reduction includes co-assembly of plasmonic and catalytic metal nanoparticles to the build-up p-n semiconductor junction. Such a geometry, will accelerate the energy of electrons and rise the photocathode potential, which is required for further improvement in the efficiency of the overall system. Moreover, it is expected that p-n junction will affect the CO<sub>2</sub> reduction products distribution in the point that main reaction products change from CO and HCOOH to hydrocarbons.

**The outcome of this project is to bring about a marked advancement in understanding of light-induced effects upon reduction of CO<sub>2</sub> at selected catalysts, such as extra activation of the process provided by the plasmonic nanostructures.**