

The use of fossil fuels (oil, coal, gas) as the main energy sources has led to adverse impacts on environment and human health. The main product of their combustion, CO₂, is considered as the main reason of climate changes and so called global warming. Increasing demands to disrupt this reliance on conventional sources energy, drive the exploration and development of clean, inexpensive, effective and renewable energy sources. Solar energy is the cleanest, inexhaustible and most abundant renewable energy source available. It was estimated that each year the Earth receives about $3 \cdot 10^{24}$ J of solar energy, and this amount is enough to cover the energy needs of all people on our Planet. The only problem is the way of its conversion and storage. One of the way is conversion into chemical energy by photocatalytic degradation of organic pollutants of water or air, while the storage may be realized by water decomposition to oxygen and hydrogen which may be stored and used as a fuels. These processes occur with the use of inorganic or organic semiconductors. Irradiation of semiconductor with photons of energy equal or higher than the band gap energy, leads to excitation of electron from the conduction to valence band and formation of the hole in the valence band. Photogenerated electron-hole pairs may undergo recombination or may reach the semiconductor/solution interface to take part in desired reactions with the solution species. Recombination strongly decreases the efficiency of photocatalytic process and therefore, the investigations are aimed at suppression of this process. Another very important requirement for high photocatalytic efficiency is appropriate location of the edges of conduction and valence bands of the semiconductor to achieve high reduction and oxidation power of photogenerated charge carriers.

An interesting approach, proposed in recent years is application of Z-scheme photocatalytic systems inspired by natural photosynthesis in plants. They are composed of two visible-light active semiconductors with such arrangement of valence and conduction bands that it facilitates a vectorial electron-transfer between both semiconductors and avoids the backward reactions by application of donor/acceptor couple in the solution or solid state mediator. The remaining electrons in one semiconductor are well separated from the holes in the other, and have reduction potential high enough to reduce protons to hydrogen and oxygen to superoxide radicals, effective in photocatalysis. On the other hand, the holes remaining in the second semiconductor can oxidize water to oxygen or hydroxyl groups to very active hydroxyl radicals.

Although the Z-scheme photocatalytic systems have a huge potential for solving energy and environmental problems, they are still at an initial stage of development. The critical issue is lack of extended studies on the interfacial charge transfer and electron-hole recombination in these rather complicated ternary systems, which are necessary for improvement of photocatalytic performance and further development in this field. This was for us a motivation to undertake the comprehensive studies in this project, focused on the kinetics of the charge separation, electron-hole recombination and charge transfer at the photocatalyst/solution interface as well as correlation of the kinetic parameters of these processes with the method of synthesis, physicochemical properties and photocatalytic activity of visible light driven Z-scheme photocatalyst. The studies will be performed for several system composed of inorganic and polymeric semiconductors without and with solid-state mediators (metal nanoparticles and carbon nanodots) which should help in controlled recombination of undesired electron-hole pairs. The studies will be focused on verification of the role of the mediator and appropriate location of conduction and valence bands in both semiconductors.

All components and hybrid system elaborated in this project will be characterized by means of microscopic (SEM, HRTEM), spectroscopic (UV-vis, FTIR, XPS) and X-ray (XRD and EDX) techniques and theoretical DFT calculations. The dynamics of the charge transfer will be studied by means of photoelectrochemical transient techniques, light intensity modulated photovoltage or photocurrent spectroscopies, a.c. impedance measurements, femtosecond pump-probe transient absorption spectroscopy and time-resolved photoluminescence. Photocatalytic activity of the elaborated systems will be tested in reaction of photodecomposition of 4-chlorophenol and dyes as well as in the reaction of photocatalytic water splitting.

The results of the studies performed in this project, will help in overcoming the problem of relatively low efficiency of the photocatalysts used so far and will be an important achievement in the field of the Z-scheme visible-light driven photocatalysts. In parallel to the development of industrial technologies, the fundamental studies on the rates of the processes occurring in the interfacial regions and dependence between the properties and photocatalytic activity of semiconductor-based systems and methods of their preparation are necessary to design the systems combining non-expensive and non-toxic materials of high catalytic activity.