Photo-Bio Production of hydrogen by [NiFe] hydrogenase-MNPs/SiO_2/M_aS_b hybrids under visible light irradiation

University of Gdansk

The aim of this project is develop **new three-layer nanostructures based on magnetic nanoparticles (MNPs) /SiO_2/metal sulfide quantum dots (M_aS_b QDs, M: Sn, Cu, Bi, In, AgIn, CuIn)** as well as connection a highly efficient hydrogen producing enzymes - [NiFe] hydrogenase to specifically engineered photocatalysts for generating hydrogen. The objective of the project is also **better understanding of the excitation mechanism and photoactivity in hydrogen production** in the presence proposed hydrogenase/nanomaterials hybrid and understanding the influence of **QDs attachment method to the surface of core/shell structure on the photocatalytic properties under visible light irradiation.**

Production of clean hydrogen fuel from water using sunlight is one of the promising solutions to address the increasing demand for energy and associated environmental concerns. One of the proposed methods to obtain hydrogen is photocatalysis in the presence of nanoparticles semiconductors and solar irradiation. Hydrogen has to be produced from water using natural energies such as sunlight if one thinks of energy and environmental issues. Therefore, achievement of solar hydrogen production from water has been urged. The basic requirements for developing and optimum photocatalysts for overall water splitting are (*i*) CB and VB edge potentials suitable for overall water splitting (*ii*) band-gap energy lower than 3 eV for visible-light harvesting (*ii*) physicochemical stability during photocatalytic reaction. Photocatalysts able to reduce water to hydrogen usually work in the UV irradiation. Therefore, a lot of studies have been performed to develop a photocatalytic system which can be activated under visible light irradiation. To achieve overall water splitting, the bottom of the conduction band must be more negative than the reduction potential of H^+ to H_2 (−0.41 V vs NHE at pH 7) and the top of the valence band must be more positive than the oxidation potential of H_2O to O_2 (0.82 V vs NHE at pH 7). The number of stable photocatalysts with these require is very small, they also work in the field of UV radiation. Many scientists are also working on the generation of hydrogen using a artificial photosynthesis process. An interesting strategy for photocatalytic production of hydrogen from water and sunlight is the formation of a hybrid photocatalyst that combines an inorganic semiconductor able to absorb in the visible light spectral range with an enzymatic catalyst-hydrogenases for reducing protons. The system composed by hydrogenase anchored to the surface of photocatalysts could be a valid alternative to typical noble metal co-catalyst in the H_2 production from solar light. Hydrogenases are the enzymes that catalyze in a reversible way the oxidation of H_2 to electrons and protons.

Based on the literature data and our own experience, it is expected that hybrids based on [NiFe] hydrogenase-MNPs/SiO_2/M_aS_b QDs will be great candidate for hydrogen generation under visible light irradiation. **The proposed three-layer nanomaterials (MNPs/SiO_2/MS) will be connected with hydrogenase by linker which allow for readily and quickly separation of the hybrid system after the reaction by the application of an external magnetic field.** The existence of the SiO_2 layer will block the direct contact between the magnetic nanoparticles and metal sulfides as a result of its wide band-gap. The metal sulfides SnS, CuS, Bi_2S_3, In_2S_3, $AgIn_5S_8$, $CuInS_2$ will be deposit on the surface MNPs/SiO_2 in the form of quantum dots (2-10 nm) because the small particle size of the photocatalyst can significantly increase the process efficiency of photocatalytic. The band gap, conduction and valence band potentials of the materials are tunable based on their particle size. The proposed metal sulfide **have the a suitable position of the conduction band necessary for the production of hydrogen and a narrow band gap** to enable excitation of three-layer materials by visible irradiation. Moreover, the suitable band gap of CuS, $AgIn_5S_8$ and $CuInS_2$ together with its strong localized surface plasmon resonance (LSPR) effect, make those materials potentially ideal as low-cost light-harvesting and charge transport material for photocatalysis.