On the mechanism of plasmonic photocatalysis

The use of solar radiation for energy, environment/water and chemistry purposes is highly needed for sustainable development. One of the methods is based on the application of photocatalysts (materials with ability to initiate chemical reactions under irradiation). However, the most active materials could use only a small portion of solar light (usually only UV range) for photocatalytic reactions, and all semiconductor photocatalysts suffer from the recombination of photogenerated electrons and holes, and thus low quantum yields of photocatalytic reactions are achieved.

Therefore, in this proposal the improved photocatalytic performance is proposed by enhanced light harvesting via plasmonic photocatalysis, i.e., photocatalysis with localized surface plasmon resonance (LSPR). The plasmon resonance was used unawares even in ancient times. For example, the Romans come across the colorful potential of nanoparticles (NPs) by accident, and thus nowadays Roman artisans are named as "the nanotechnology pioneers" – they impregnated the glass with particles of silver and gold, ground down until they were as small as 50 nm in diameter. In Europe, the most popular plasmonic properties of metallic NPs could be seen in beautiful stained-glass windows in the oldest churches (one probable example shown below in Fig. 1 (left)). It should be pointed out that the observable color depends on the properties of noble metals' NPs (size and shape), and thus the controllable change in the morphology results in the preparation of samples with different photoresponse (Fig. 2 (right)).

Although the research on plasmonic photocatalysis is popular, and many reports have already been published, the mechanism of plasmon-assisted catalysis is still under extensive discussion. In this project, plasmonic photocatalysts with different properties will be developed to clarify the mechanism of plasmonic photocatalysis, and to propose the key-factor features for efficient, stable and novel materials for solar-driven reactions. Many advanced methods and techniques will be used to achieve this goal, including the study in the collaboration with foreign partners, such as action spectra analysis, photoacoustic spectroscopy (PAS), reverse-double beam photoacoustic spectroscopy (RDB-PAS), 3D-finite-difference time domain (3D-FDTD) simulations, time-resolved microwave conductivity (TRMC), electron spin resonance (ESR) spectroscopy, light-intensity dependent activity tests, etc.



Fig. 1. The photographs of: [left] the stained-glass window from The Church of St. Casimir the Prince in Kraków, Poland (Red and yellow/brown colors could result from NPs of gold and silver, respectively.); [right] gold NPs of different sizes with exemplary SEM images for four corresponding samples.