Investigating the mechanisms and efficiency of green hydrogen formation as a by-product of the photoreduction of carbon dioxide in the aqueous and gas phases

Hydrogen is evolving as an energy solution due to high costs and stringent regulations. However, with government support, hydrogen can become a revolutionary solution that will play a key role in the energy transition, transport and business. Implementing more friendly regulations and developing and continuing research and innovation can make a significant difference in realising the full potential of hydrogen. However, hydrogen production involves the formation of pollutants (including carbon dioxide), which are most often emitted into the air. The strategy of the European Green Deal is making a decisive contribution to positive change in this respect. However, reports by the Stockholm Environment Institute (SEI) and Oxfam (*Confronting Carbon Inequality*) show that, globally, there has been a dramatic increase in emissions of carbon dioxide and other harmful gaseous pollutants (up to 393 million tonnes of CO_2 equivalent per year) in 2022 as a result of increased activity by companies belonging to just the richest 1% of the world's population (in 2022 it was 125 people). Undoubtedly, the rapidly growing emissions in different regions are strikingly unequal. Increasingly stringent limits on CO_2 emissions into the air have never been or are either no longer respected by many emerging countries.

The PhotoH2 project concept proposes an answer to the question of how to combat by small "scientific" steps the growing inequality in terms of carbon dioxide emissions across world regions while at the same time fitting in with the principles of a circular economy and policies of compound recovery, clean technologies or Carbon Capture and Utilisation (CCU) technologies. Innovative and pro-environmental technological solutions, which include the design and synthesis of new-generation materials with high pollutant removal efficiency by converting them into valuable products (in this case, hydrogen as a by-product of water splitting, as well as CO and CH_4 as products of the CO_2 photoreduction reaction), while meeting most of the principles of green chemistry, are important from both an energy and environmental sustainability point of view. By photocatalytic reduction of CO_2 gaseous pollutants in the aqueous and gas phases (with access to water vapour) and in the presence of TiO_2-based materials, it is also possible to obtain end products, such as green hydrogen, which, in the era of the "hydrogen revolution," represents a significant added value to the project. Therefore, the overarching goal of the project will be to determine the potential for using the photocatalytic water decomposition reaction to produce green hydrogen as a side reaction accompanying the aqueous or gas phase (with a small amount of water) CO_2 photoreduction process.

Due to the fundamental nature of the project, mechanisms accompanying the processes will be understood in detail. It should be emphasised that the proposed concept could be classified as a "2-in-1" solution on several levels. Firstly, the photocatalytic water splitting (as a side reaction) will produce green hydrogen, and simultaneously, the degradation of CO_2 in the photoreduction reaction will yield valuable products. Secondly, the advantages of two phenomena will be exploited here: the adsorption of CO_2 by microporous carbon carriers (as solid supports of modified titanium dioxide thin films), and photocatalysis, through which H_2, CO and CH_4 can occur. Thirdly, titanium dioxide thin films will be obtained by reactive magnetron sputtering with simultaneous modification of TiO_2 with bimetallic/double-oxide compositions (simultaneous modification with two types of metal ions (including Al, Ag, Au, Cu, Pt, Pd, Ni, Ru) or their oxides.

It is important that thanks to the experience of Prof. Kamila Kočí and her team from VSB - Technical University of Ostrava, it will be possible to extend the research to the aqueous phase (in which the Czech team specialises), in addition to carrying out the hydrogen generation reaction accompanying the photoreduction of CO_2 in the gas phase (with a small amount of water), which the Polish team specialises in. The cooperation will also enable a more detailed characterisation of the materials obtained, including the results of photoelectrochemistry, XRF analysis and temperature-programmed desorption/reduction (TPD/TPR) to determine active sites. Conducting these studies at ZUT would require the commitment of additional financial resources.

The PhotoH2 project offers an exceptional platform for young researchers and post-docs from both VSB-TUO and WPUT in Szczecin to enhance their skills and expand their knowledge in a truly international environment. Researchers will gain invaluable experience through exchange research internships at partner institutions, where they will engage in experimental work, collaborate with peers from diverse research environments, and learn directly from leading scientists in materials preparation, characterisation, and photocatalytic processes. The involvement of young researchers in the project's activities not only enriches their academic and professional growth but also allows for a more thorough and multifaceted investigation of the mechanisms and efficiency of green hydrogen formation as a by-product of the photoreduction of carbon dioxide in both aqueous and gas phases. Integrating diverse expertise ensures a holistic approach to tackling one of the most pressing challenges in sustainable energy research.