M.Radecka, Black/Blue TiO_2 for green hydrogen generation-game of colors?

The contemporary world faces the energy crisis, being at the same time a driving force for development of novel, renewable and environment friendly sources of “fuel of the future”. Hydrogen as a powerful energy carrier is very attractive alternative to the existing standard solutions. Particularly, “green hydrogen” which is produced *via* H_2O splitting by sunlight into H_2 and O_2, is based uniquely on natural resources, *i.e.*, water and SunExtensive research on integrated solar-driven photoelectrochemical cells for “green hydrogen” generation has been carried out since 1972 when TiO_2 has been used for the first time as a photoanode providing absorption of the incident light [1].

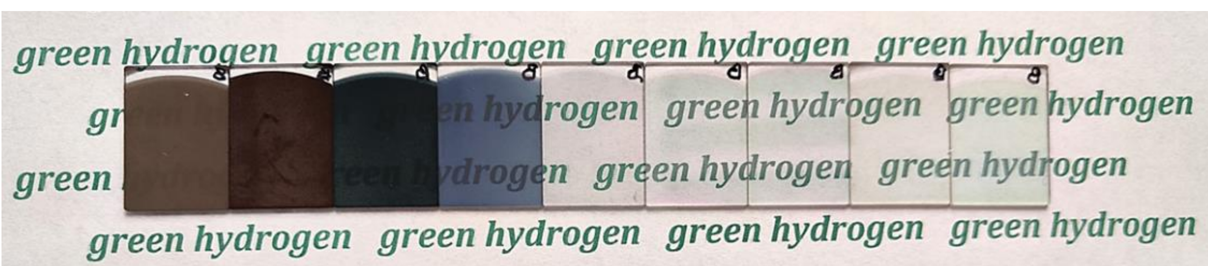
In 1995, in view of little progress on solar-to-hydrogen efficiency remaining much lower than 10%, the construction of “*an efficient and long-lived system for splitting water to H_2 and O_2 with light in the terrestrial (AM1.5) solar spectrum at an intensity of one sun*” has been considered as a Holy Grail in chemistry [2].

At the moment, however, this aim is far from being reached in simple systems. The reason for this failure lies mostly in poor adaptation of the available metal oxide semiconductors acting as auxiliary light absorbers, i.e., photoelectrodes, to the solar spectrum and significant difference between the lifetime of the generated photoelectrons and holes and the time required for the redox reaction at the photoanode-electrolyte interface.

The aim of the project is to develop a new strategy involving the use of selectively disordered titanium dioxide for photodecomposition of water. The main focus of the research will be black and blue TiO_2 nanostructures, which show strong absorption in the visible and near-infrared light range, which are:
- black TiO_2 with a core-shell structure as a result of surface reduction (disordered shell)
- blue TiO_2-a mixture of rutile and anatase with ordered/disordered phases through selective reduction.

Phase-selective defected titanium dioxide, obtained in the form of thin films and nanopowders, will be used to produce green hydrogen as:
- semiconductor photoanode in a PEC photoelectrochemical cell
- nanoparticles for photocatalytic water reduction using methanol.

Below are photos of TiO_2 thin films prepared by reactive magnetron sputtering when sputtering a metallic target in an oxygen-containing atmosphere [3]. You can clearly see the color evolution: from black to white when increasing the oxygen content in the $Ar+O_2$ mixture.



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[2] A.J. Bard, M.A. Fox, Artificial photosynthesis: solar splitting of water to hydrogen and oxygen, Acc.Chem. Res. 28 (1995) 141–145. https://doi.org/10.1021/ar00051a007
[3] [3] Płacheta, K., Kot, A., Banas-Gac, J.Zajac, M.,Sikora, M., Radecka, M., Zakrzewska, K. Evolution of surface properties of titanium oxide thin films, Applied Surface Science, 2023, 608, 155046. https://doi.org/10.1016/j.apsusc.2022.155046