

Photoelectrochemical Splitting of Saline Water

Jurga Juodkazytė*, Milda Petrulevičienė, Irena Savickaja, Rimantas Ramanauskas

Center for Physical Sciences and Technology, Saulėtekio av. 3, Vilnius, Lithuania

*jurga.juodkazyte@ftmc.lt

Photoelectrochemical (PEC) conversion of solar energy into chemical energy, known as artificial photosynthesis, is becoming increasingly popular because of its potential to produce value-added chemicals such as hydrogen, carbon-based fuels, oxidants, etc. The products of PEC reactions can be fine-tuned by rational choice of photoelectrode and electrolyte. The use of seawater as a virtually inexhaustible water resource and nature's ready-to-use electrolyte for solar energy conversion and storage is a growing area of research. The most abundant anions in seawater are chlorides (55%) and sulfates (~28%). These anions can be photoelectrochemically oxidized to strong oxidants such as reactive chlorine and sulfate species (RCS and RSS). In this context, deep valence band (VB) semiconductors are of particular interest due to their ability to generate highly oxidizing holes (h^+). The VB potentials of tungsten (VI) oxide, WO_3 , and bismuth vanadate, $BiVO_4$, are ~3 V and ~2.5 V (vs SHE), respectively, which means that photogenerated holes have enough energy to drive oxidation reactions via the formation of highly reactive radical species as intermediates (Figure 1). In hole scavenging processes, anions compete with water molecules. The kinetics and selectivity of possible photoanodic reactions in such systems depend strongly on the nature, morphology and architecture of the photoelectrodes as well as pH of the electrolyte. PEC formation of RCS (ClO^- , ClO_2^-) and RSS ($S_2O_8^{2-}$) on WO_3 and $BiVO_4$ photoelectrodes in chloride and sulfate medium with Faradaic efficiencies ranging between 50 and 100 % were found.¹⁻³ Factors determining the performance of these semiconductors in PEC splitting of saline water will be discussed and the potential applications of artificial photosynthesis will be demonstrated.

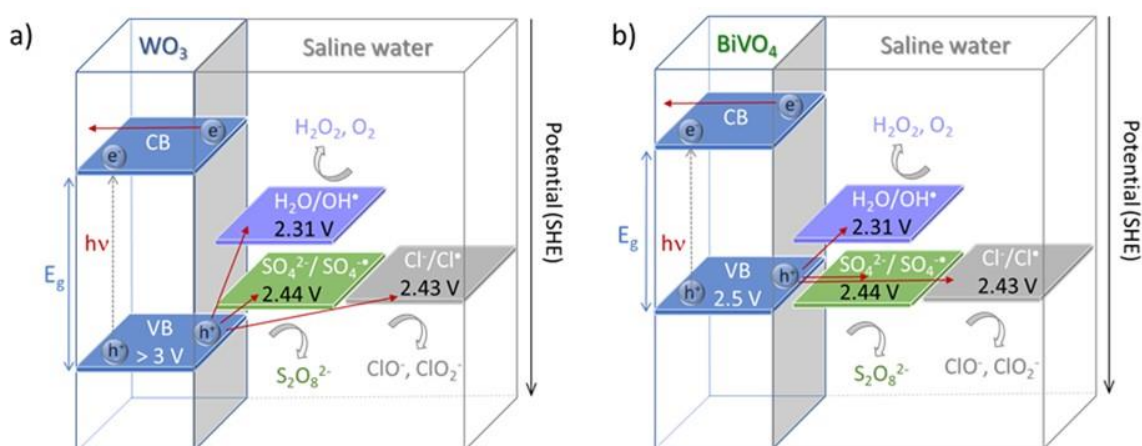


Figure 1: Schematic representation of possible hole-induced photoanodic processes at a) WO_3 and b) $BiVO_4$ photoanodes in aqueous chloride and sulfate solutions at pH 7, illustrating different potential of h^+ to drive specific reactions; VB - valence band, CB - conduction band, E_g - energy band gap, $h\nu$ - photon energy; the energy levels are not drawn to scale, they are intended to serve as a visual guide

Acknowledgements

This research was funded by the M-ERA.NET project “Multiscale computer modelling, synthesis and rational design of photo(electro)catalysts for efficient visible-light-driven seawater splitting”(CatWatSplit), Reference Number: project8168, under a grant agreement Nr. S-M-ERA.NET-21-3 with the Research Council of Lithuania (LMTLT).

References

1. M. Parvin, M. Petrulevičienė, I. Savickaja, B. Šebeka, R. Karpicz, A. Grigučevičienė, R. Ramanauskas, J. Juodkazytė *Electrochim. Acta*, 2022, **403**, 139710. <https://doi.org/10.1016/j.electacta.2021.139710>
2. M. Petrulevičienė, I. Savickaja, A. Grigučevičienė, A. Naujokaitis, R. Ramanauskas, J. Juodkazytė, *J. Photochem. & Photobiol. A: Chemistry*, 2023, **443**, 114842. <https://doi.org/10.1016/j.jphotochem.2023.114842>
3. M. Parvin, I. Savickaja, S. Tutlienė, A. Naujokaitis, R. Ramanauskas, M. Petrulevičienė, J. Juodkazytė, *J. Electroanal. Chem.*, 2024, **954**, 118026. <https://doi.org/10.1016/j.jelechem.2024.118026>