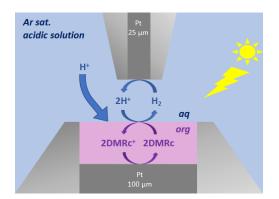
H₂ photogeneration at droplet placed on recessed electrode

Ariba Aziz¹, Wojciech Nogala¹, Marcin Opallo^{1†}

¹Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224, Warszawa, Poland † corresponding author's email: mopallo@ichf.edu.pl

Light-driven HER at liquid|liquid (LL) interface with metallocene as electron donor is a strategy to reduce protons without additional photosensitizer [1,2]. Here, we will demonstrate a system allowing the decrease of the volume of the organic phase and continuous electrochemical recycling of the electron donor. For this purpose, a droplet of decamethylruthenocene (DMRc) solution in trifluorotoluene (TFT) was placed on a recessed Pt microelectrode in contact with aqueous acid. LL interface was chemically polarized by dissolving different salt of highly hydrophobic tetrakis(pentafluorophenyl) borate anion (TB⁻) in both phases to ensure proton transfer from aqueous to organic phase [3]. This system differs from that earlier proposed, because it does not require precise positioning of the microelectrode below LL interface [4] and cancerogenic 1,2-dichloroethane was replaced by TFT [5].

SECM was employed for the detection of generated hydrogen. Substrate generation/tip collection mode was applied in an Ar saturated acidic solution, whereas feedback mode was used in H₂ saturated neutral electrolyte. In both conditions, hydrogen was detected above an organic droplet in the presence of light.



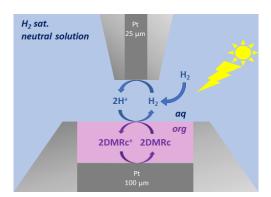


Figure 1: Schemes of detection of H₂ photogenerated at liquid|liquid interface with electrochemical recycling of electron donor.

Acknowledgments

Financial support by the National Science Centre (NCN, Poland) through grant UNISONO Solar-Driven Chemistry (DFG) No. 2019/01/Y/ST4/00022.

References

- [1] L. Rivier, T.J Stockmann, M.A Méndez, M.D Scanlon, P. Peljo, M. Opallo and H.H Girault, *J. Phys. Chem C* 119 25761 (2015).
- [2] L. Rivier, P. Peljo, L.A.C. Vannay, G.C. Gschwend, M.A. Mendez, C. Corminboeuf, M.D. Scanlon and H.H. Girault, *Angew. Chem. Int. Ed.* **56** 2324 (2017).
- [3] I. Hatay, B. Su, F. Li, R. Partovi-Nia, H. Vrubel, X. Hu, M. Ersoz and H. H.Girault, *Angew. Chem. Int. Ed.* 48 5139 (2009).
- [4] J. Jedraszko, W. Adamiak, W. Nogala, H. H. Girault and M. Opallo, J. Electroanal. Chem. 819 101 (2018).
- [5] W. Adamiak, J. Jedraszko, O. Krysiak, W. Nogala, J.C. Hidalgo-Acosta, H.H. Girault, and M. Opallo, J Phys Chem C 118 23154 (2014).