Effect of the Anchoring Groups on the Photostability of Ruthenium(II) Polypyridyl Sensitizers

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Introduction

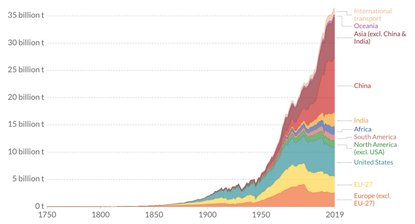


Figure 1. Global emissions of carbon dioxide[1]

- Carbon dioxide emissions are the primary driver of global climate change. Producing more energy from renewable resources is a good choice to reduce CO_2 emissions.
- Using solar power to generate hydrogen in water splitting system can be a sustainable approach to produce energy from renewable resources.

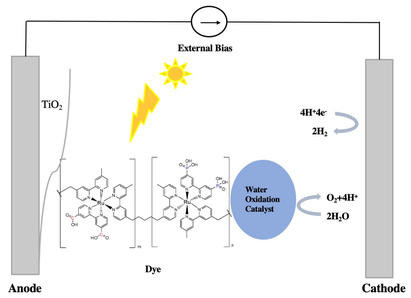


Figure 2. The structural design of a WS-DSPEC[2]

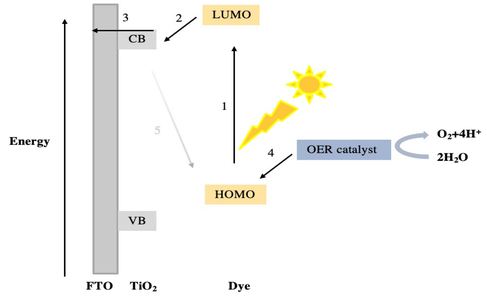


Figure 3. Simplified electron transfer scheme on the photoanode[3]

Results and discussion

1. Photostability measurements

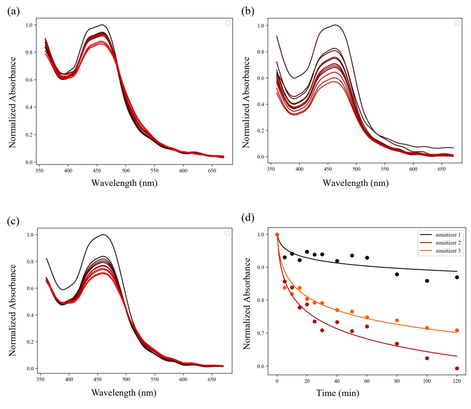


Figure 6. Absorbance of sensitizers at pH 4.9

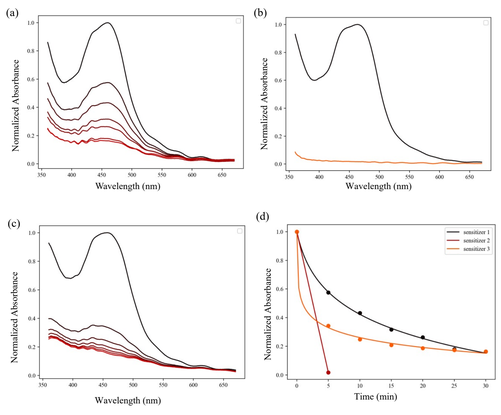
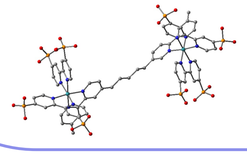


Figure 7. Absorbance of sensitizers at pH 6.9

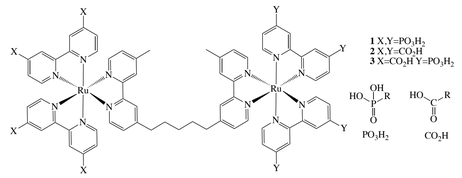
2. Geometry optimization of sensitizer **1**

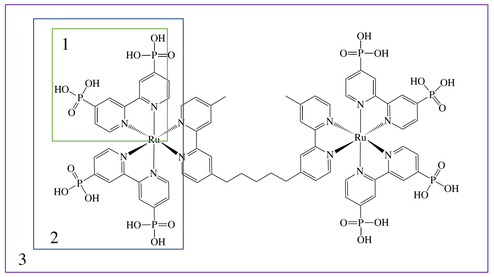


- The binding mode through the carboxylate or phosphonate groups.
- How the number of anchors (phosphonate or carboxylate groups) on the sensitizers affects the binding stability on TiO_2 surface?

Experimental Design

1. Synthesis of sensitizers





2. Photoanode preparation

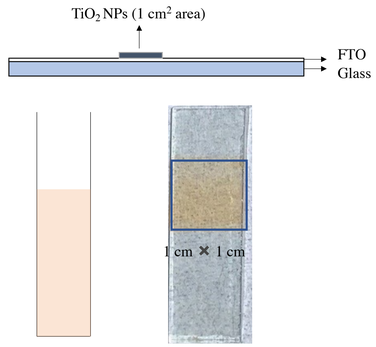


Figure 4. The process of photoanode preparation

3. Photostability measurements

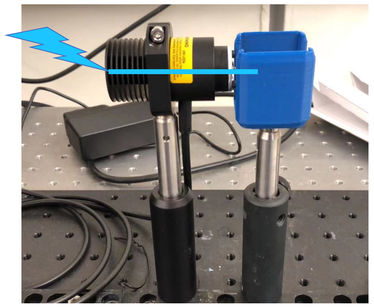


Figure 5. Photostability measurements

4. Theoretical calculations

- H, C, N ,O, P: The B3LYP functional and 6-31G basis sets; Ru: The LANL2DZ
- The geometries are optimized in the gas phase without counterions.

Conclusion

- Sensitizer **1** with all phosphonate groups shows the best photostability among three sensitizers from pH 4.9 to pH 6.9 under the constant light irradiation (10 mW/cm^2).
- The presence of phosphonate anchors enhances the photostability of sensitizers on TiO_2 electrodes compared to the carboxylate.

1. Our World in Data based on Global Carbon Project. https://ourworldindata.org/co2-emissions. (accessed Mar 30, 2021)
2. Gray, C.L.; Xu, P.; Rothenberger, A.J.; Koehler, S.J.; Elacqua, E.; Milosavljevic, B.H.; Mallouk, T.E. An Oligomeric Ruthenium Polypyridyl Dye for Improved Stability of Aqueous Photoelectrochemical Cells. *The Journal of Physical Chemistry C* **2020**, *124*, 3542-3550.
3. Swierk, J.R; Mallouk, T.E. Design and development of photoanodes for water-splitting dye-sensitized photoelectrochemical cells. *Chemical Society Reviews* **2013**, *42*, 2357-2387.