Photocatalytic hydrogen production via bioinspired heteroleptic* Nickel catalysts

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Amid the global energy crisis, the demand for alternative energy resources aimed at achieving a greener and more sustainable future is rapidly increasing. In this context, hydrogen technologies emerge as a promising zero-emission energy source with significant potential for energy storage. To address the energy barrier of the water-splitting redox reaction [1], we draw inspiration from NiFe-hydrogenase enzymes to develop biomimetic catalysts[2]. Additionally, NiFeSe-hydrogenase[3], which incorporates selenocysteine instead of cysteine at the enzyme's active site, opens new avenues for synthesizing a diverse range of catalysts that include either selenium or both selenium and sulfur in their ligand frameworks.

Furthermore, the well-established non-innocent character of these ligands enhances the stabilization of their complexes due to the ligands' aromatic coordination structures. These natural catalysts achieve the highest known yield for the electrochemically reversible reaction of proton/hydrogen interconversion[4]. Light-driven hydrogen evolution through photocatalysis under LED lamps ($\lambda \geq 400$ nm) creates conditions conducive to artificial photosynthesis (AP), paving the way for a greener and more circular energy economy[5]. In this study, we present the synthesis and characterization of a series of new heteroleptic Ni complexes as catalysts, along with their efficiency in visible light-driven hydrogen production. Furthermore, the role of the ligands' substituents is examined.

References

[1] Li, Xiao, et al. Nano-Micro Letters12, 1-29 (2020).

[2] Pintus A., et al. Coordination Chemistry Reviews 464, 214444 (2022).

[3] Wombwell, C., et al. Acc. Chem. Res. 48, 2858–2865 (2015)

[4]Evans, et al. Journal of the American Chemical Society (2024)

[5] Kamatsos F., International Journal of Hydrogen Energy 46.37, 19705-19716 (2021).