High activity metalloenzymes for sustainable production of fuels

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Most catalysts used for critical chemical transformations such as producing \( \text{H}_2 \), reducing \( \text{CO}_2 \) or \( \text{N}_2 \), rely mainly on expensive and rare precious metals or energy intensive processes, strongly reducing the sustainability of associated technologies. Intensive research is addressing the development of alternative catalysts based on earth abundant materials, but efficiencies and selectivities are still far from desired. In nature these difficult transformations involving multi-electron and multi-proton reactions, are achieved by enzymes containing metal cofactors, which display outstanding catalytic efficiencies in mild conditions and using abundant metals. Many of these enzymes are oxygen-sensitive and susceptible to degradation, but recent technologies are remarkably extending the lifetime of these biocatalysts. Here we will present the characterisation of two remarkable metalloenzymes, a NiFeSe-hydrogenase\(^1\) and W/Sec-formate dehydrogenase\(^2\), both of which are highly active and show remarkable oxygen stability, as well as some variants with improved properties\(^3\). The \( \text{O}_2 \) stability and robustness of these enzymes has been exploited for the development of efficient semi-synthetic photo- and electrocatalytic systems\(^4,5\), and are also the basis for whole-cell photocatalysis\(^6\).

\(^3\) Zacarias S; Temporão A; del Barrio M; Fourmond V; Leger C; Matias P & Pereira IAC 2019 ACS Catalysis, 10, 3844–3856.
\(^6\) Martins M, Toste C, Pereira IAC Angewandte Chemie Int. Ed. 2021 60, 9055-9062