The Biological H_2 Conversion: Pitfalls and Potentials of Hydrogenase Enzymes

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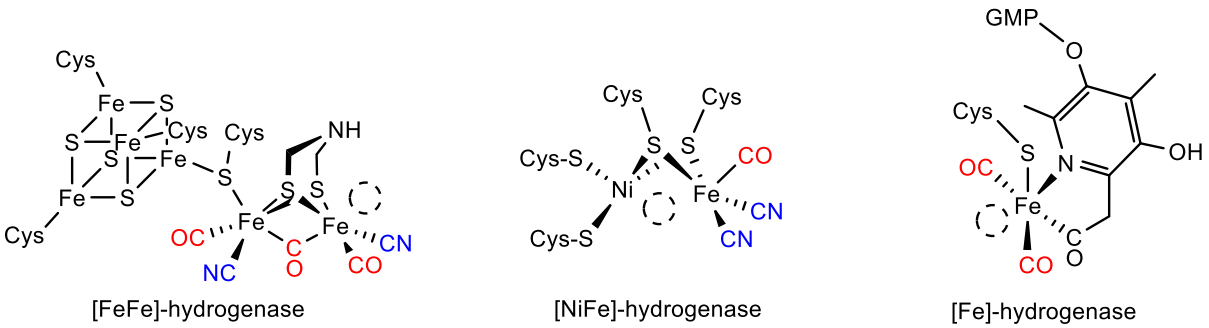
There is a general agreement that the building of a sustainable hydrogen economy, based on the combined development of photoelectrolyzers (for energy storage through water splitting into dihydrogen and dioxygen) and of fuel cells (for converting H_2 and O_2 back into electricity) in part relies on the availability of cheap, abundant, and efficient catalysts. The discovery of hydrogen-metabolizing enzymes, hydrogenases, and subsequent understanding of their structure and chemistry have been major breakthroughs towards novel catalytic strategies aimed at replacing platinum, currently used in the technological devices mentioned above.[1,2] Not only hydrogenases work with remarkably high catalytic rates at the thermodynamic equilibrium but also these metalloenzymes employ first row transition metals, nickel and/or iron, within their active sites (**Figure**).[3] The talk will give a general overview of the biological H_2 conversion, highlighting the role played by hydrogenases as well as pitfalls of ongoing research on these enzymes. Finally, a few examples showing promising achievements using hydrogenases will be illustrated.



[FeFe]-hydrogenase [NiFe]-hydrogenase [Fe]-hydrogenase

Figure. Schematic representation of the H_2-converting active sites found in hydrogenases. The dashed circle highlights the open coordination site used to bind H_2. Cyanide (CN) and/or carbon monoxide (CO) ligands coordinate the Fe ions in all three hydrogenase classes.

References:

1. Lubitz, W., Ogata, H., Rüdiger, O. & Reijerse, E. Hydrogenases. *Chem. Rev.* **114**, 4081–4148 (2014).

2. Caserta, G., Roy, S., Atta, M., Artero, V., Fontecave, M. Artificial hydrogenases: biohybrid and supramolecular systems for catalytic hydrogen production or uptake. *Curr Opin Chem Biol.* **25**,36-47 (2015).

3. Britt, R. D., Rao, G. & Tao, L. Bioassembly of complex iron–sulfur enzymes: hydrogenases and nitrogenases. *Nat. Rev. Chem.* **4**, 542–549 (2020).