Engineered metalloenzymes for aqueous proton reduction

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The development of hydrogen (H_2) as an environmentally friendly fuel requires catalysts capable of efficient proton reduction. Ideally, these catalysts would be active in water near neutral pH, insensitive to oxygen, and insensitive to added ions and impurities. Biomolecules are attractive scaffolds to use for engineering artificial hydrogenases because of their compatibility with aqueous media and the wide range of derivatives that can be accessed using site-directed mutagenesis and protein chemistry. In this presentation, progress toward the development of biomolecular hydrogen evolution catalysts will be presented. One class contains cobalt porphyrin active sites that display high activity and stability at neutral pH in the presence of air. Turnover numbers of over 200,000 have been achieved under electrocatalytic conditions. Another class of catalysts consist of easily assembled metallopeptides proposed to have a proton shuttle site. To demonstrate successful solar energy storage, photosensitizers have been paired with catalysts to yield thousands of turnovers. Ongoing refinements are toward further increasing stability and lowering overpotential by engineering catalyst structure.