One step forward to understand the biological reduction of CO\textsubscript{2} to formate by Mo/W formate dehydrogenases

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The reversible interconversion of CO\textsubscript{2} into formate by Mo/W-Formate dehydrogenases (Fdhs) placed these enzymes on the spotlight. Probing a promising route not only for green gas sequestration but also a sustainable way to produce fuel.

FdhAB is a periplasmic heterodimer and the main responsible for CO\textsubscript{2} reduction in \textit{D. vulgaris} (Dv) \cite{1}. It comprises a pyranopterin cofactor in the active site (W-bisMGD, selenocysteine and a sulfido ligand) and four [4Fe4S] clusters responsible for electron transfer. Contrary to other Fdhs, this enzyme is oxygen-tolerant and can be purified aerobically \cite{2}. Due to its robustness and high catalytic activity, \textit{Dv}FdhAB is a suitable model for biocatalytic applications for CO\textsubscript{2} reduction. Biochemical and structural studies on \textit{Dv}FdhAB unveiled oxidized and reduced forms of the enzyme and unique features related to its robustness (Fig. 1) \cite{2,3}.

\textbf{Figure 1.} W-FdhAB catalysed reduction of CO\textsubscript{2} to formate

The requirement for its pre-activation with reducing agents led us to consider a disulfide bridge 23 Å away from the active site. C843A and C872A mutants hinder the formation of this disulfide and were shown to be catalytically like the pre-activated wild-type enzyme in the absence of reducing agents, leading to the proposal that this disulfide bridge might work as a redox switch for enzyme activation and O\textsubscript{2} protection \cite{4}.

Structural studies disclosed relevant conformational changes promoted by the absence of the disulfide and results and mechanistic implications will be presented.


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