Role of the Non-protein Ligand at the Ni-Fe Active Site of [NiFe] Hydrogenase

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Hydrogenases catalyze oxidoreduction of molecular hydrogen and have a potential value for a use of dihydrogen as an energy source.

[NiFe] hydrogenase possesses two oxidized states, Ni-A (inactive) and Ni-B (active). The pure Ni-A state was successfully prepared from the solution of the as-purified enzyme (mixture of the Ni-A and Ni-B states), and the crystal structures of both the Ni-A and Ni-B states have been determined at ultra-high resolution. The shape and size of the electron densities show that Ni-B possesses a monatomic non-protein bridging ligand between the Ni and Fe atoms at the active site and the cysteine sulfur ligand (Cys546) was modified by unknown atomic species (X546). Whereas Ni-A has a diatomic ligand at the bridging site and two systein sulfur ligands (Cys546 and Cys84) were also modified by unknown species (X546 and X84). X546 of Ni-A was shifted towards the Ni atom about 1.0 Å compaired to that of Ni-B. Diatomic bridging ligand and X84 of Ni-A seem to block the pathway of dihydrogen.

The essential features of the enzyme structure at the resting state and the transition mechanism from Ni-B to Ni-A are proposed.

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