Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

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Light-induced reactivation of O_2-tolerant membrane-bound [Ni-Fe] hydrogenase from the hyperthermophilic bacterium *Aquifex aeolicus* under turnover conditions

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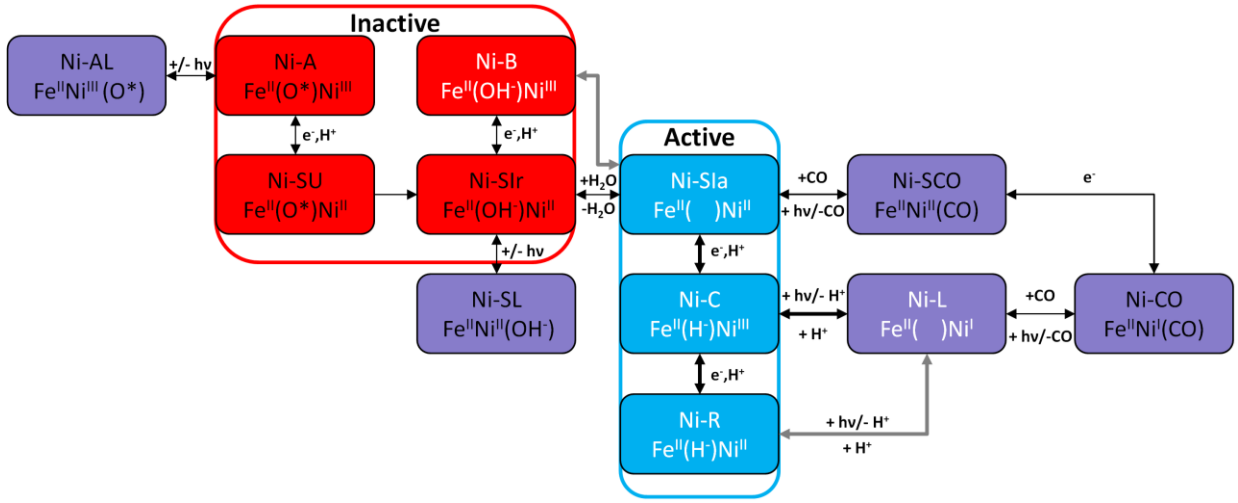

Fig. S1 Synthesized scheme gathering the different redox states spectroscopically identified for the [Ni-Fe] active site of O_2-tolerant and O_2-sensitive hydrogenases reported from the literature [1-10]. Redox states observed in O_2-tolerant hydrogenases are highlighted in white policy. Active, inactive and photo-induced states are shown in blue, red and purple respectively. Thin arrows represent redox transitions observed only in O_2-sensitive hydrogenases. Bold black arrows represent redox transitions observed in both O_2-tolerant and O_2-sensitive hydrogenases. Bold grey arrows represent redox transitions specific to O_2-tolerant hydrogenases. (O*) represents the unknown oxygenic ligand.

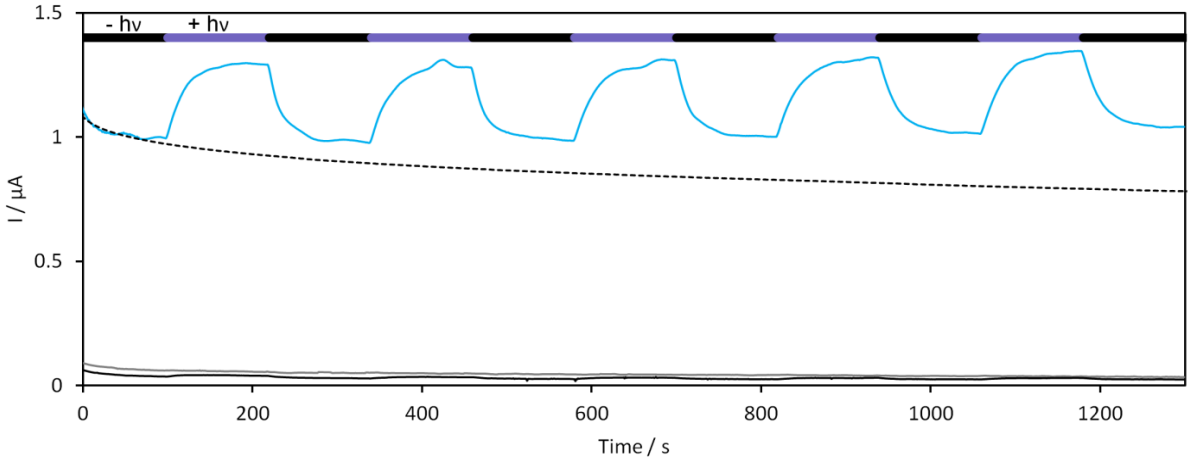

Fig. S2 Typical CA experiments for MbH1 under H_2 (blue curve) and under N_2 (grey curve) and CA experiment at bare PG electrode (black curve), with five consecutive illumination/darkness steps represented by the black/purple sequence. CA of MbH1 under H_2 and darkness is superimposed (dotted black curve).These CA experiments are recorded at E = -0.1V *vs.* Ag/AgCl, 50 mM HEPES, pH 7.2, 60°C, H_2 atm.

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