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【174】 Co-Pyrphyrin on $\text{Cu}_2\text{O}(111)$ and $\text{TiO}_2(110)$: Properties and Stability under Near Operando Conditions

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Cobalt-pyrphyrin (Co-Pyr) is a promising water reduction catalyst. $\text{Cu}_2\text{O}(111)$ and $\text{TiO}_2(110)$ with monolayer coverage of Co-Pyr were studied for pressures spanning from UHV up to 1mbar of water vapor. Under UV illumination, surface photovoltage shifts of $\Delta E_k = +120\text{meV}$ are observed on $\text{Cu}_2\text{O}(111)$. X-ray absorption spectroscopy of the Co L3-edge was used to monitor the electronic structure of the molecule's metal center. Comparison to simulated spectra reveals that on $\text{TiO}_2(110)$, the Co centers partially transform from a +2 to +1 oxidation state upon exposure to water, while on $\text{Cu}_2\text{O}(111)$ they remain in the +2 oxidation state. Our measurements provide insights into properties of Co-Pyr under conditions near those in solar fuel cells.

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