

Heterogeneous Second-Sphere Coordination Modified Iron Porphyrin for Carbon Dioxide Reduction

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Carbon monoxide dehydrogenase (CODH), an enzyme found in some anaerobic bacteria, is capable of reducing reversibly and selectively CO₂ to CO with a high reaction rate and almost no overpotential.[1] Inspired by the active site of this enzyme (Figure 1), we had previously developed an iron-porphyrin catalyst (**FeUr**, Figure1) for the homogenous electrocatalytic reduction of CO₂. [2] The urea groups introduced in the second coordination sphere of this biomimetic catalyst were shown to play a similar role to that of amino acid residues found in the second coordination sphere of the CODH active site. This role consists of establishing multiple hydrogen bonds to increase the catalyst affinity for CO₂ bonding and stabilize reactive intermediates. The second coordination sphere brought a significant improvement in the overpotential of the CO₂ electrocatalytic reduction compared to the non-functionalized iron-tetraphenylporphyrin (**FeTPP**, Figure 1) while keeping a good selectivity and high reaction rate.

Homogenous catalysis has a practical advantage when it comes to performing spectroscopic studies to better understand the reaction mechanism or to introduce structural modifications on the catalyst.[3] However, the electrocatalytic reaction is generally performed in organic solvents and takes place only in the first diffusion layer of the electrode which limits the scale-up of the reaction. To take our catalyst one step further toward an industrial application for CO₂ reduction, we developed a new modified electrode by immobilizing the **FeUr** catalyst on carbon paper using multiwall carbon nanotubes (MWCNT) (Figure 1). Our results show that the second coordination sphere effect can be transposed to heterogeneous catalysis for electrocatalytic reduction of CO₂ in water. We also demonstrated that the **FeUr**-modified electrode displays better selectivity and four times higher current density than that of **FeTPP**-modified electrode.

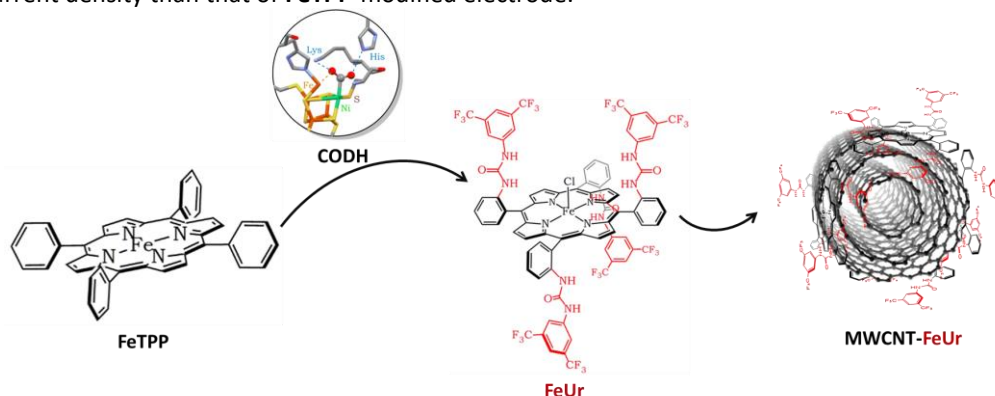


Figure 1. Introduction of urea groups in the second coordination sphere of iron porphyrin and its heterogenization.

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