

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

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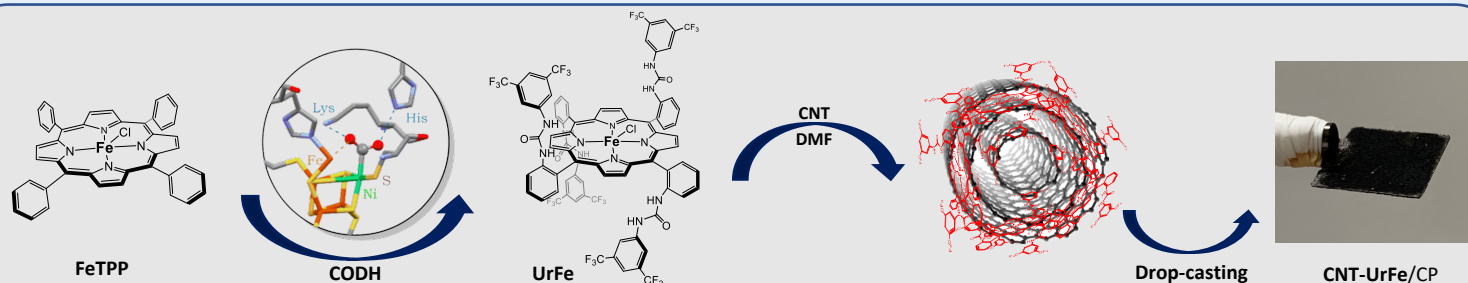
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I. Introduction

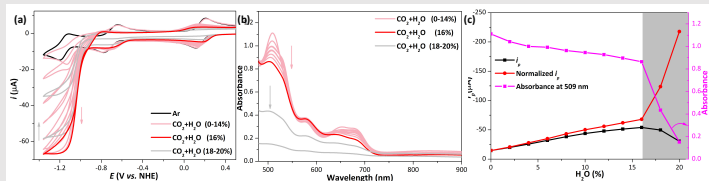
- Carbon monoxide dehydrogenase (**CODH**) can selectively and reversibly convert CO₂ to CO with high reaction rate and almost no overpotential.¹ In our previous research, inspired by **CODH** enzyme active site, we have developed an urea modified iron porphyrin (**UrFe**) for homogeneous electrochemical reduction of CO₂.² The multi-hydrogen bond on the second coordination sphere of **UrFe** can promote the CO₂ binding ability and stabilize CO₂ intermediates in DMF. The overpotential for CO₂ reduction by **UrFe** significantly decreased when keeping high reaction rate and selectivity.
- Though **UrFe** exhibited excellent catalytic performance for CO₂ reduction, the homogeneous catalysis is generally performed in organic solvent and **UrFe** is only active on the first diffusion layer. In the perspective of a practical application, we immobilized **UrFe** catalyst on carbon paper using multi-wall carbon nanotubes (MWCNT) and studied its performance for CO₂ reduction in water.

II. Catalyst Heterogenization



III. Electrocatalytic Evaluation

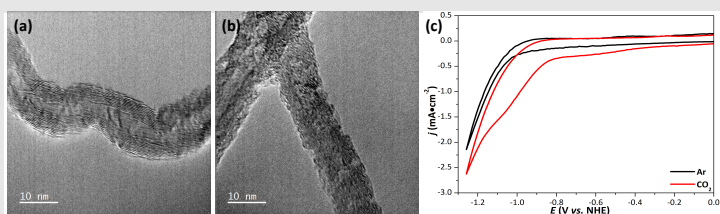
Effect of water in homogeneous catalysis



CV, UV-vis and the correlated i_p , absorbance at 509 nm of **UrFe** in DMF containing different amount of H₂O.

- The maximum catalytic current intensity is reached around 16% H₂O.
- UV-Vis analysis of **UrFe** at different H₂O proportion in DMF indicates that the current intensity decrease because of the precipitation of **UrFe** due to its hydrophobicity.

UrFe Modified electrode



TEM of MWCNT, **CNT-UrFe** and CV of **CNT-UrFe/CP** in 0.1 M NaHCO₃ aqueous solutions.

- TEM** shows a morphology change of MWCNT from smooth to wrinkled wall verifies the incorporation of **UrFe** on MWCNTs.
- Compared with CV under Ar, **CNT-UrFe** catalyst under CO₂ shows a significant increase in the reductive current at a potential more negative than -0.4 V vs. NHE.
- The bulk electrolysis coupled with GC analysis of **CNT-UrFe/CP** suggests that the highest selectivity of CO (99.9%) can be obtained at -0.78 V vs. RHE.
- Stable current densities are observed at -0.48 V to -0.88 V vs. RHE during 2 hours electrolysis.

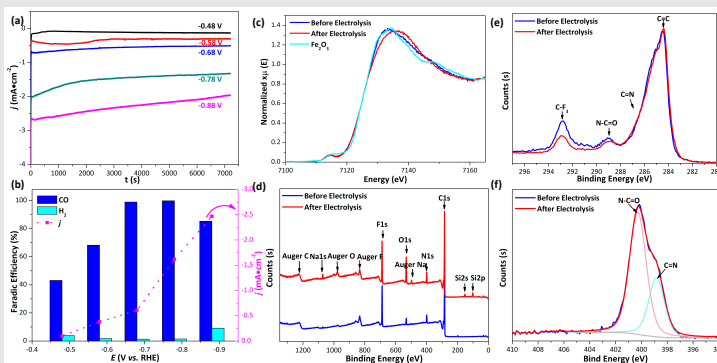
IV. Conclusion

- H₂O is the a sufficient proton source in CO₂-saturated DMF for CO₂ electroreduction by **UrFe**. However, because of its hydrophobicity, the catalyst precipitates when the water content exceeds 16%.
- CNT-UrFe** exhibits stable current densities and the highest selectivity of CO was 99.9% in water. The XPS and XANES analysis of **CNT-UrFe/CP** suggests there is no significant degradation during bulk electrolysis.
- Under the same conditions, **CNT-UrFe** shows four times higher current density than that of **CNT-FeTPP**. Moreover, **CNT-UrFe** displays a higher FE_{CO} of 90.8% than that of **CNT-FeTPP** (58.6%).

V. Reference

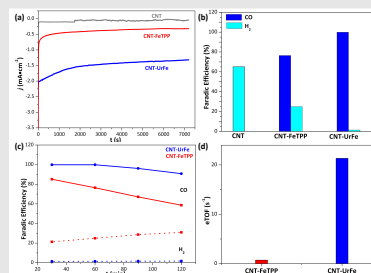
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- Gotico P., Boitrel B., Guillot R., Sircoglou M., Quaranta A., Halime Z., Leibl W., Aukauloo A., *Angew. Chem. Int. Ed.*, **2019**, 58 (14), 4504-4509.

The XPS and XANES analysis of **CNT-UrFe/CP** before and after electrolysis suggests that there is no significant degradation during the 2 hours electrolysis.



Bulk electrolysis of **CNT-UrFe** in CO₂-saturated 0.1 M NaHCO₃ aqueous solutions, XANES and XPS spectra of **CNT-UrFe** before and after electrolysis.

Second sphere effect in heterogeneous catalysis



Bulk electrolysis of **CNT**, **CNT-UrFe** and **CNT-FeTPP** at -0.78 V vs. RHE in CO₂-saturated 0.1 M NaHCO₃ aqueous solutions.

- CNT-UrFe** exhibits four times higher current density than that of **CNT-FeTPP**. However, **CNT-FeTPP** still has much higher current density than non-modified **CNT**.
- GC analysis after a 2 hours electrolysis reveals that FE_{CO} is 90.8% in the case of **CNT-UrFe** and only 58.6% in the case of **CNT-FeTPP**.
- The effective turnover frequency (eTOF) of **CNT-UrFe** is 21 s⁻¹, which is more than one order of magnitude higher than that of **CNT-FeTPP** (0.9 s⁻¹).