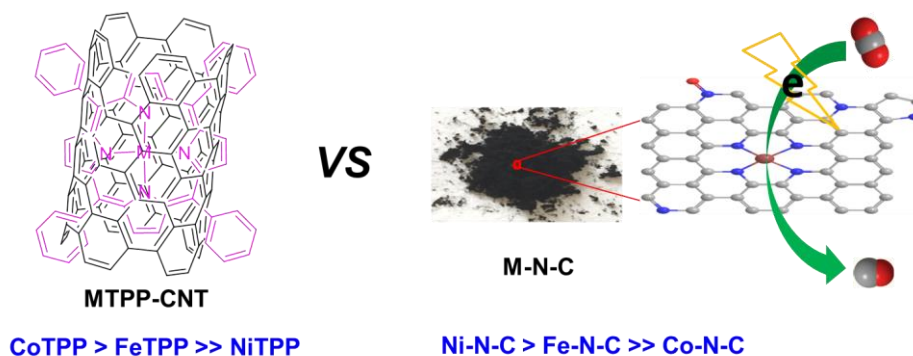


Selective CO₂ Reduction to CO in Water using Earth-Abundant Metal and Nitrogen-Doped Carbon Electrocatalysts

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Metalloporphyrins immobilized on carbon materials have been proved to be catalytically active for CO₂ electroreduction in neutral water.[1,2] The porous carbon materials installed with metalloporphyrin-like structures are expected to be more promising due to their large surface area, high conductivity, and good chemical stability.[3] In this work, we synthesized a series of Earth-abundant transition metal (Fe, Co, or Ni) and nitrogen doped porous carbon electrocatalysts (M-N-C) from cheap precursors via silica templated pyrolysis.[4] The effect of the material composition and structure (i.e. porosity, nitrogen doping, metal identity, and oxygen functionalization) on the activity for electrochemical CO₂ reduction reaction (CO₂RR) was investigated. The metal-free N-C exhibits a high selectivity but low activity for CO₂RR. Incorporation of the Fe and Ni, but not Co, sites in the N-C material is able to significantly enhance the activity. The general selectivity order for CO₂-to-CO conversion in water is found to be Ni > Fe >> Co with respect to the metal in M-N-C, while the activity follows Ni, Fe >> Co. Notably, the Ni doped carbon exhibits a high selectivity with a faradaic efficiency of 93% for CO production. Tafel analysis shows a change of the rate-determining step as the metal overtakes the role of the nitrogen as the most active site. Recording of X-ray photoelectron spectra and extended X-ray absorption fine structure demonstrates that the metals are atomically dispersed in the carbon matrix, most likely coordinated to four nitrogen atoms and with carbon atoms serving as a second coordination shell. Presumably, the carbon atoms in the second coordination shell of the metal sites in M-N-C significantly affect the CO₂RR activity, since the opposite reactivity order is found for carbon supported metal meso-tetraphenylporphyrin complexes (MTPP). From a better understanding of the relationship between the CO₂RR activity and the material structure it becomes possible to rationally design high-performance porous carbon electrocatalysts involving Earth abundant metals for CO₂ valorization.



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