Green and Cheap Hemin-based Electrocatalyst for selective CO_2-to-CO conversion

Matteo Miola[1], Steen Uttrup Pedersen[1], Kim Daasbjerg[1], Troels Skrydstrup[1],

Annette-E. Surkus[2], Henrik Junge[2] and Matthias Beller[2]

[1] *Carbon dioxide activation centre at Aarhus University, Aarhus, Denmark*
[2] *Leibniz Institute for Catalysis at the University of Rostock, Rostock, Germany*

Aarhus University, The iNANO House, Gustav Wieds Vej 14, 8000 Aarhus C, Denmark
matteo.miola@inano.au.dk

The release of carbon dioxide (CO_2) and other greenhouse gases (GHGs) into the atmosphere due to human activities affects severely the global climate. Among the GHGs, CO_2 accounts for 82.2% of the total emission and e.g. reached 5.4 BMT in 2015 in US alone.[1] Nevertheless, from a chemical point of view CO_2 can be considered as a non-toxic, highly available, and cheap C1 feedstock. In particular, the electrochemical carbon dioxide reduction reaction is a scalable approach that can be powered by renewable energy sources and offers the generation of a plethora of products, i.e. CO, CH_4, CH_3OH, HCOOH, and longer-chain hydrocarbons.[2] A key issue consists of identifying selective and active catalysts that will lower the energy barrier and exert control on the product distribution. Recently, nitrogen doped carbon materials containing MN_x (M= Fe, Co, Ni) have shown high activity and selectivity towards the electrochemical reduction of CO_2 to CO.[3] The main draw backs of these syntheses are the numerous steps involved and the low atom efficiency, nullifying the low-cost catalyst claim. In this work we developed a green and low-cost catalyst for the electrochemical CO_2-to-CO conversion. The material is based on hemin, a highly available, green, and cheap Fe(III) protoporphyrin IX that is directly obtainable from animal blood extractions and supported on commercially available carbon powder. The synthesis involves only aqueous solvents and one pyrolysis step without further processing (Fig. 1A). Electrolysis carried out at –1.2 V vs Ag/AgCl in 0.5 M $KHCO_3$ using this material gave a Faradaic efficiency of >99% for the CO_2-to-CO conversion with a current density of 3.15 mA cm^{-2} after 15 min, declining to 98% and 1.90 mA cm^{-2}, respectively, after 4 h. Analysis by X-ray photoemission spectroscopy, transmission electron microscopy, X-ray diffraction, and electrochemical methods revealed the specific effects that the hemin absorption on the carbon support and the pyrolysis protocol had on the catalytic activity. Finally, the Fe(II)N_xC centers were identified as the catalytic sites.

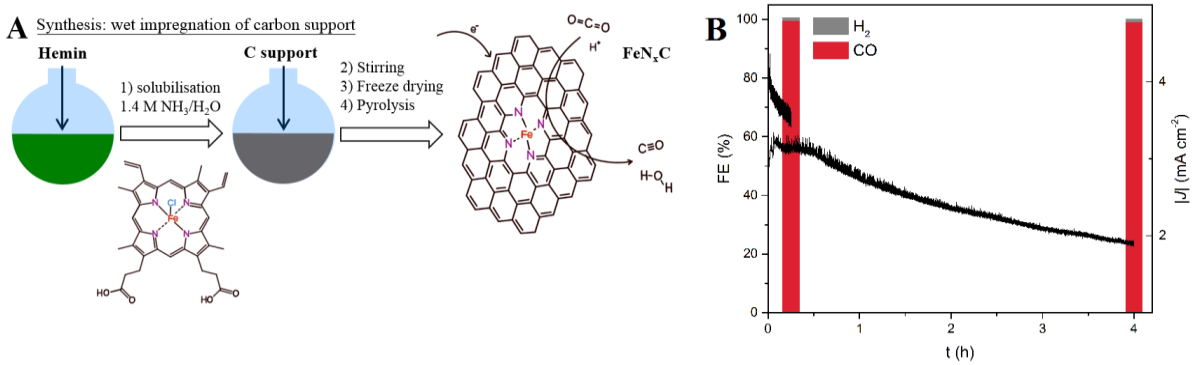

Figure 1. A) Synthesis protocol of FeN_xC materials from the pyrolysis of hemin and B) faradaic efficiency (left axis) and current density (right axis) recorded in a 4 h electrolysis at –1.2 V vs Ag/AgCl in 0.5 M $KHCO_3$.

References

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