Porous single atom electrocatalysts with high electrochemical active site utilization

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Metal single atoms in nitrogen doped carbon materials (M-NC) have attracted plenty of attention during the last decades in the field of electrocatalysis for oxygen reduction and carbon dioxide conversion amongst others. In the cathode of proton exchange membrane fuel cells Fe-NC are the most promising solution to scarce and expensive Platinum-group-metal catalysts,[1] and in the cathode of CO_2 conversion electrolysers, Fe and Ni-NC are predicted to be as active as Au or Ag.[2] However, their controlled synthesis and stability for practical applications remains challenging due to the high temperature pyrolysis step that results on Fe aggregation and formation of oxides and carbides. Decoupling high temperature pyrolysis and the Fe coordination, can circumvent the disadvantages of the high temperature pyrolysis,[3] nevertheless, the metal utilization within these materials remains very low owing to the lack of scaffolds that combine adequate micro- and mesoporosity.

In this work we employ inexpensive 2,4,6-Triaminopyrimidine (TAP) with $MgCl_2.6H_2O$ as porogen to prepare a highly porous N-doped carbon material.[4] The hydrogen bonding between nitrogen moieties of TAP and the water molecules of the Mg salt allows an optimal interaction during pyrolysis that leads to remarkable porosity in the nitrogen-doped material (~3300 $m^2\ g^{-1}$) and very available N sites for Fe or Ni coordination. The subsequent low temperature metal coordination (Figure 1) results in a highly active O_2 reduction electrocatalyst with a mass activity 4.0 A g^{-1} at 0.8 V_{RHE} in acid electrolyte, and one the highest turnover frequency for CO_2 reduction reported to date for M-NC materials.[5] Additionally *in-situ* nitrite stripping reveals a high active site density of $>2\times10^{19}$ sites g^{-1}; and a electrochemical active site utilisation of 52% and 76% for Fe and Ni-NC, respectively, up to our knowledge the highest reported to date.

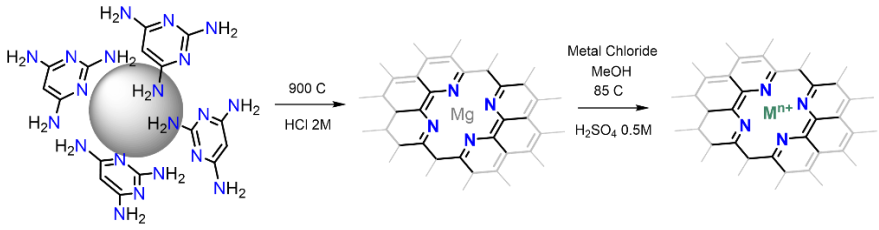

Figure 1. Schematic representation of the templated synthesis of a porous single atom electrocatalysts.

References

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