

WATER OXIDATION

Relying on a relay*Nat. Commun.* **10**, 5074 (2019)

Electrocatalytically oxidizing water to form oxygen is one half of the overall water splitting reaction that generates hydrogen fuel in an electrolyser. In the past, molecular water oxidation catalysts have been designed that make use of ligand–substrate interactions away from the main metal site where the catalysis occurs, in the so-called second coordination sphere. However, in heterogeneous water oxidation catalysts such effects are not as well understood. Now, Fusheng Li, Licheng Sun and colleagues at Dalian University of Technology and KTH Royal Institute of Technology present a highly active heterogeneous water oxidation catalyst based on second coordination sphere effects and elucidate their role in the activity.

The researchers synthesize a catalyst based on a Ni–Fe terephthalate coordination polymer, which contains both metal-coordinated and uncoordinated carboxylate groups. For comparison, they also prepare a Ni–Fe layered double hydroxide catalyst, which does not contain any carboxylate groups. Once surface area effects have been taken into account, the Ni–Fe terephthalate coordination polymer is found to have the superior performance of the two catalysts. The researchers' experimental results suggest that concerted proton-coupled electron transfer plays an important role in the catalysis for both samples. However, in further studies — including kinetic isotope effect, proton inventory and atom-proton transfer experiments — the researchers find that the two catalysts behave differently. The results suggest that the uncoordinated carboxylate groups can act as proton relays in the second coordination sphere of the Ni–Fe terephthalate coordination polymer and lead to its enhanced catalytic activity.

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