Host-guest interactions on electrode surfaces for immobilization of molecular catalysts

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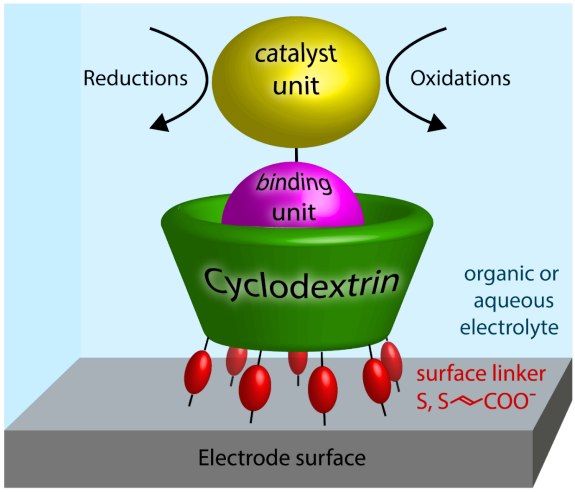
Connecting molecules to (photo-)electrode surfaces is one of the main challenges for molecular approaches in catalytic transformations driven by renewable resources such as sunlight. Classical grafting strategies include anchoring groups to bind the molecules onto the substrates, functionalization onto carbon-based materials as well as polymer scaffolds to fix catalysts close to the electrode surface [1]. However, many of these grafting methods suffer from drawbacks such as unstable binding to the surface, complicated synthesis and purification of ligands and decrease of activity due to necessary modifications of the catalysts [2].

We propose a new approach that relies on host-guest complex formation, a highly specific form of non-binding interactions, using modified cyclodextrin molecules as surface-bound host domains. We demonstrate the simple preparation of molecularly functionalized electrodes, facile catalyst adaptation to carry a guest domain and that electrocatalysis with these systems can be performed efficiently in water or organic solvent. Using spectroscopic and surface sensitive characterization methods as well as computational simulations, we show that the catalyst molecules are attached to the surface via their guest-substituent binding group as a host-guest complex with the cyclodextrin. Electrochemical measurements demonstrate that electron transfer to the guest metal center leads to catalysis in both organic and aqueous electrolyte systems. Furthermore, the surface-bound cyclodextrin hosts can be recycled to bind fresh catalytic guests. This makes host-guest interactions a very attractive method for attaching molecular catalysts onto both metal and metal-oxide electrode supports.



[1] Zhang, B. & Sun, L., *Chem. Soc. Rev.*, **2019**, 48, 2216.
[2] Liu, X., Inagaki, S. & Gong, J., *Angew. Chem. Int. Ed.*, **2016**, 55, 14924.