

Modelling catalyst materials for CO₂ reduction: from metal nanoparticles to halide perovskites

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Two urgent, interconnected problems of our times are the exhaust of conventional energy resources and the need to reduce CO₂ emissions and move towards a sustainable carbon emission free economy. Environmentally-friendly reduction of CO₂ to fuels might serve as a solution to both problems. The use of electrocatalysis or photocatalysis for this reaction will result in green fuel production that could rely on renewable energy sources alone. Up to now, CO₂ reduction is at the forefront of catalysis science and is challenged by selectivity and stability issues in the existing catalytic materials and processes.

Aiming to design optimized anode materials for electrochemical CO₂ reduction to fuels, our quest on electrocatalytic CO₂ reduction is twofold; we explore the catalytic properties of two classes of materials, transition metals and perovskite semiconductors, by means of first principles calculations. Our starting point is the best-known catalyst for CO oxidation towards CO₂, which is gold nanoparticles [1]. We employ Density Functional Theory (DFT) calculations and the Nudged-Elastic Band (NEB) method to locate reaction transition states and identify minimum-energy paths (MEPs) for chemical reactions on 10-atom gold nanoclusters. We discuss energetics of the reactions and provide insight into the conditions that favour one reaction over the other, thus helping improving catalyst selectivity. We compare to standard CO₂ reduction catalysts such as single-crystal Cu.

For the second family of materials, metal halide perovskites and their 2D structures and nanostructures have emerged in the last decade as superb semiconducting materials, mainly driven by their high output in photovoltaics. Many side applications have already branched out, with one being their applications in electrocatalytic and photocatalytic fuel cells [2]. Due to their superior optical absorption and their ability to operate for a wide range of bandgaps depending on how one varies their chemical composition [3], metal halide perovskites can be tailored to the needs of each specific photoelectrocatalytic process. We mainly focus on 2D perovskites with bulky hydrophobic cations between the sheets of corner-connected octahedra. We perform DFT electronic-structure calculations for such systems and comment on their potential uses in environmentally-friendly catalytic processes.

References

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