Well-defined hybrid Copper-based nanoreactors for electrocatalytic CO2 reduction

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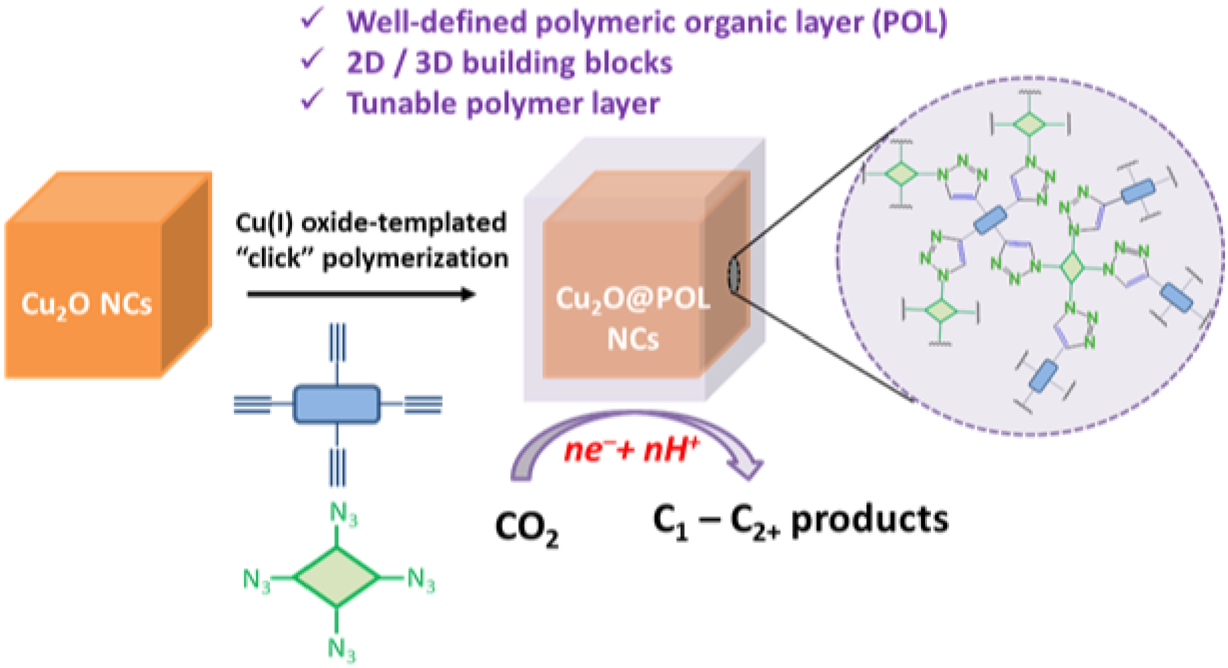

In the perspective of drastically reducing anthropogenic CO_2 emissions and mitigating the effects of global warming, the electrochemical CO_2 reduction reaction (CO_2RR) powered by renewable sources and catalyzed by transition metal-based catalysts represents an attractive strategy to produce fuels and commodity chemicals. However, further improvement in the catalyst design is required to tackle the main bottlenecks that currently limit the performances of the state-of-the-art catalysts. Although several transition metal-based systems have been reported to catalyze CO_2RR,[1]-[2] catalyst durability and selectivity still represent major challenges to achieve an efficient CO_2RR, mainly due to catalyst deactivation and to competitive Hydrogen evolution reaction (HER) and/or alternative pathways leading to multiple carbon-based products.

The combination of molecular chemistry and heterogeneous catalysis has recently revealed to be an effective strategy to improve the overall efficiency and selectivity of the CO_2RR process.[3] In particular, the formation of hybrid catalysts based on the integration of organic molecules or reticular frameworks with heterogeneous metal or metal-oxide surfaces allowed to tune the stability of key reaction intermediates or the local microenvironment of the catalyst, resulting in a significant improvement of the CO_2RR performances.[4]-[5]

In this contribution, we highlight a modular and versatile strategy to synthesize well-defined hybrid nanomaterials, based on the in situ growth of polymeric matrices around a well-defined metal nanoparticle core in a controlled manner. For instance, well-defined Cu_2O nanocubes (NCs) are used as both templates and catalysts for an in situ polymerization based on a Cu-catalyzed azide–alkyne cycloaddition reaction (CuAAC) in the presence of the corresponding monomeric building blocks.[6] This approach results in a series of hybrid nanoreactors with well-defined shape and size, which are active electrocatalysts for CO_2 reduction in neutral-pH electrolyte. The composition of the molecular layer was found to be critical for the catalytic performances. The data herein presented provide a proof-of-concept of the potential offered by a molecular perspective towards a rational design of heterogeneous electrocatalysts.

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