Towards the selective and energy-efficient synthesis of ethylene via carbon dioxide reduction

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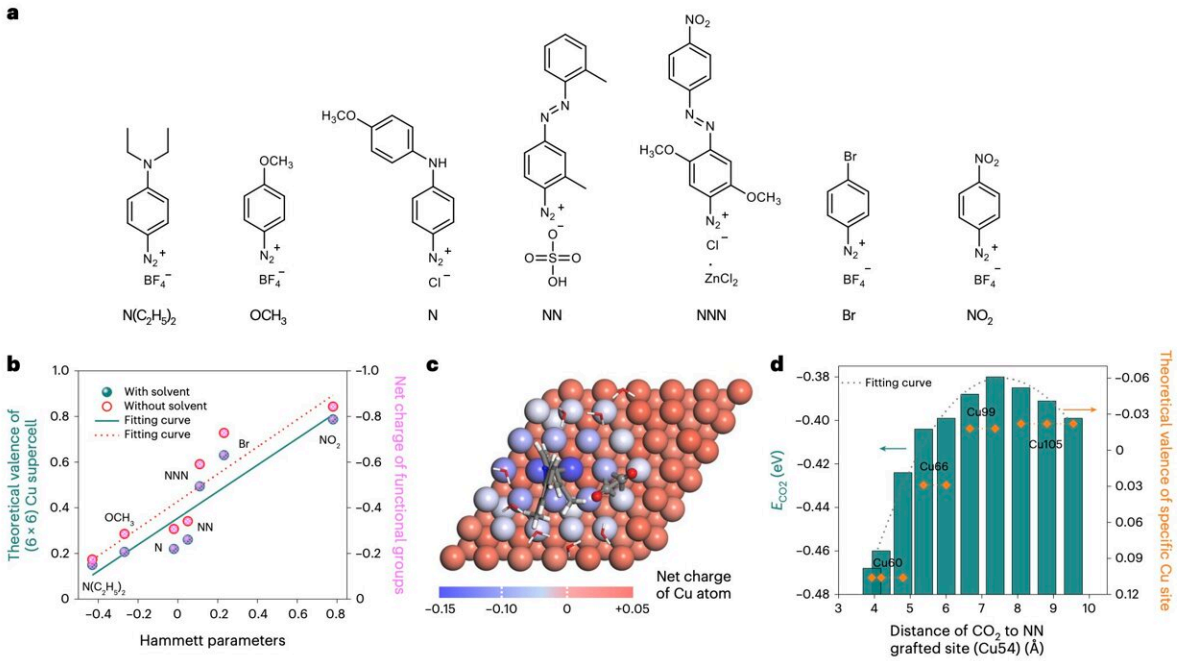

DFT simulations. a, Molecular structures of different diazonium salts. b, The relationship between the theoretical valence of the whole (6 × 6) Cu supercell and the electro-withdrawing ability of different substitutes on phenyl according to Hammett parameters21,22. c, Heat map of the valence of the top Cu atoms near the NN functional group calculated considering explicit water. Cu, N, C and O atoms are illustrated as orange, blue, grey and red balls, respectively, whereas water molecules and NN are shown as lines. The lowest and the highest net charge of Cu atom is −0.15 (purple) and +0.05 (erythrinus). d, The relationship between the distance of adsorbed CO2 to the NN grafted copper atom (Cu54),

the theoretical valence (right y axis, dot plots) of CO2-adsorbed specific Cu sites (Cu60, Cu66, Cu99 and Cu105) and the related CO2 adsorption energy (ECO2) (left y axis bar charts) on CO2-adsorbed Cu sites. Credit: Wu et al. (Nature Energy, 2024).

The synthesis of carbon-based chemicals via the electrochemical reduction of carbon dioxide (CO_2) has become the key objective of numerous recent energy research efforts. While these studies have yielded promising results, enabling the production of various widely used chemicals, most proposed approaches exhibit poor energy efficiencies and selectivity.

Proposed methods for the electrochemical reduction of CO_2 into the hydrocarbon ethylene, for instance, have so far not achieved desirable energy efficiency and stability. This has prevented their widespread deployment as alternatives for conventional petrochemical approaches to produce ethylene, which have adverse effects on the environment.

Researchers at Université Montpellier and other institutes recently set out to facilitate the selective and energy-efficient synthesis of ethylene via the reduction of CO_2 by functionalizing catalysts that prompt reduction reactions. Their paper, published in *Nature Energy*, introduces a strategy to functionalize copper (Cu) catalysts for CO_2 reduction using aryl diazonium salts, colorless substances currently employed to synthesize various organic compounds.

"Although progress has been made in producing multi-carbon products from the electrochemical reduction of CO_2, the modest selectivity for ethylene (C_2H_4) leads to low energy efficiency and high downstream separation costs," Huali Wu, Lingqi Huang and their colleagues wrote in their paper. "We functionalize Cu catalysts with a variety of substituted

aryl diazonium salts to improve selectivity towards multi-carbon products."

In their calculations and experiments, Wu, Huang, and their collaborators found that different aryl diazonium salts could help to tailor the oxidation state of Cu. Using these salts, they were thus able to functionalize catalysts into a membrane electrode assembly (MEA) cell, the primary component of fuel cells that facilitates desired electrochemical reactions, including the reactions underpinning the reduction of CO_2.

The researchers tested the performance of this MEA flow cell with tailored Cu sites in a series of experiments. They found that their functionalization strategy enhanced the energy efficiency and stability of CO_2 reduction to produce ethylene.

"Using computation and operando spectroscopy, we find that Cu surface oxidation state (δ^+ where 0