High-efficiency catalyst enhances the electric reduction performance of carbon dioxide

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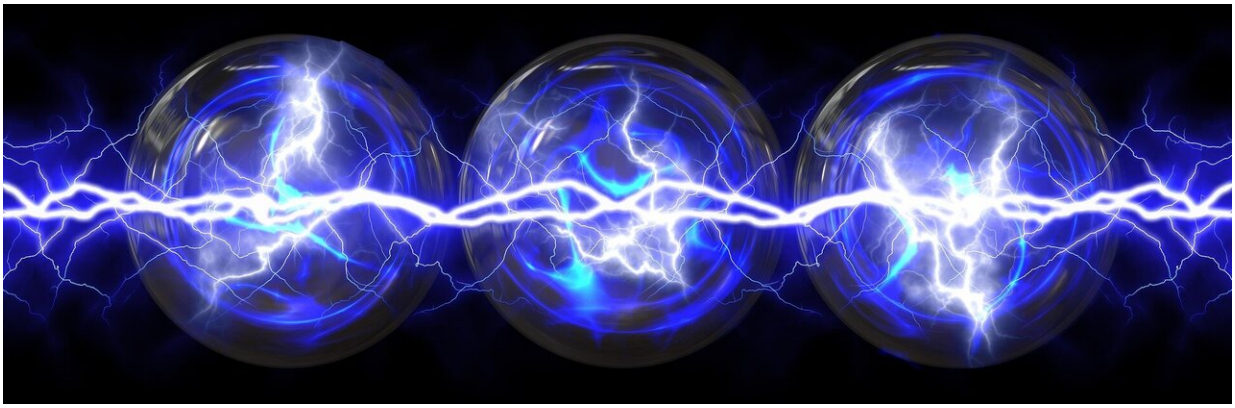

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Electrochemical conversion of carbon dioxide (CO_2) into fuels and value-added feedstocks, ideally if powered by renewable electricity, provides a route to reduce greenhouse gas emissions and simultaneously close the carbon loop. At present, the rational design and controllable synthesis of more efficient catalysts, combined with the understanding of the catalytic mechanism, in order to achieve the industrial application of CO_2 electric reduction technology has become the research focus and difficulty.

Recently, a team led by Prof. YU Shuhong and Prof. GAO Minrui from University of Science and Technology of China (USTC) of the Chinese

Academy of Sciences (CAS) developed a microwave heating strategy for synthesizing a transition metal chalcogenide nanostructure that efficiently catalyzes CO_2 electroreduction to carbon monoxide (CO). These results were published in *Angewandte Chemie* and the *Journal of the American Chemical Society*.

A considerable challenge in the conversion of CO_2 into useful fuels comes from the activation of CO_2 to CO_2- or other intermediates, which often requires precious metallic catalysts, high overpotentials, and/or the electrolyte additives (e.g., ionic liquids).

In this study, the researchers reported a microwave heating strategy for synthesizing a transition metal chalcogenide nanostructure that efficiently catalyzes CO_2 electroreduction to CO. They achieved a record CO_2-to-CO conversion current of 212 mA cm^{-2} at selectivity of ~95.5% and potential of -1.2 V versus a reversible hydrogen electrode (RHE) in a flow cell configuration by using the cadmium sulfide (CdS) nanoneedle arrays as electrocatalysts.

Experimental and computational studies showed that the high-curvature CdS nanostructured catalyst with a pronounced proximity effect gives rise to large electric field enhancement, which can concentrate alkali metal cations and thereby results in the enhanced CO_2 electroreduction efficiency.

In addition to using the "near-neighbor effect" of the nano multi-needle tip to achieve the enrichment of target ions, Prof. GAO Minrui's group and academician YU Shuhong's team further proposed using the "confined-area effect" of the nanocavity to enrich the reaction intermediates and realize the high-efficiency conversion from CO_2 to multi-carbon fuels.

The results introduced a simple confinement route for new CO_2

reduction reaction (CO_2RR) catalyst design. Spatial confinement of the in situ generated carbon intermediates within Cu2O cavities was found to be sufficient for preventing Cu+ reduction under CO_2RR and to stabilize Cu oxidation state.

They showed experimentally that the as-designed Cu_2O with multi-cavities yields C_2^+ compounds with a Faradaic efficiency of over 75% and a C_2^+ partial current density of 267 ± 13 mA cm^{-2}. Such notable C_2^+ production enabled by the catalyst demonstrated here suggested a material structuring way to boosting CO_2RR activity and selectivity for value-added carbon-based fuels powered by renewable energy.

The research shows that the design of the catalyst nanostructure in the CO_2 electroreduction reaction has an important impact on the catalytic performance. The nanoscale "enrichment effect" can effectively enhance the adsorption of key intermediates, thereby promoting the efficient operation of the reaction. This new design concept provides new ideas for the design of related electrocatalysts and the synthesis of high value-added carbon-based fuels in the future.

More information: Peng-Peng Yang et al, Protecting Copper Oxidation State via Intermediate Confinement for Selective CO2 Electroreduction to C2+ Fuels, *Journal of the American Chemical Society* (2020). DOI: 10.1021/jacs.0c01699

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