An efficient strategy to promote novel products on Cu-based catalysts

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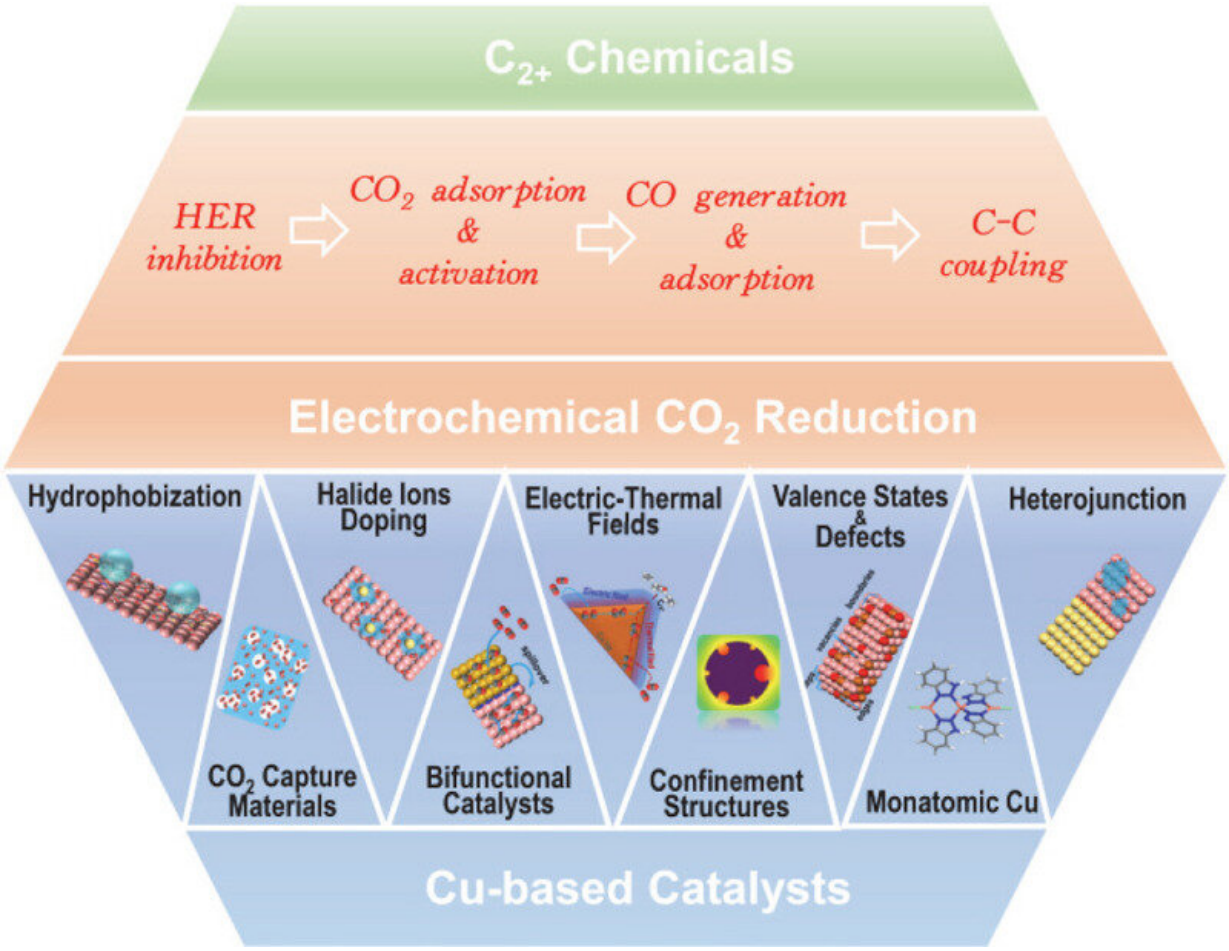

Graphical AbstractThere are four important steps of inhibition of HER, CO_2 adsorption and activation, CO generation and adsorption, and C–C coupling, need to be considered for promoting CO_2RR-to-C_{2+}. Based on this, surface modifaction of Cu-based electrodes includes hydrophobization, incorporating CO_2 capture materials, halide ions doping, enhancing electric-thermal field, and

designing bifunctional catalysts, confinement structures, oxidation states, defects, monatomic Cu, and heterojunction structures. Credit: *Chinese Journal of Catalysis* (2023). DOI: 10.1016/S1872-2067(23)64429-8

The electrochemical CO_2 reduction reaction (CO_2RR) to high-value-added products with two or more carbons (C_{2+} products) provides a viable strategy to close the anthropogenic carbon cycle and increase economic efficiency. Cu is generally considered to be the most effective active metal that exhibits notable catalytic performances for CO_2RR-to-C_{2+}.

The rationally designed Cu-based electrocatalysts for CO_2RR have been extensively developed. However, direct conversion of CO_2 to C_{2+} products with high selectivity and efficiency is still a formidable challenge because of complex reaction networks. In particular, precise control of the products to a specific C_{2+} product with high selectivity has not been achieved.

So far, it still lacks the systematic guiding laws of catalysts surface regulation to improve C_{2+} productivity. This is needed to deeply get insight into the reaction mechanism of CO_2RR-to-C_{2+} on surface and/or interfaces. Thus, a comprehensive review covering achievements on surface state modification, which could influence the catalytic performances, for high-efficiency CO_2RR-to-C_{2+} is high desired.

Recently, a research team led by Prof. Qun Xu from Zhengzhou University, China, summarized the recent advances in surface engineering of Cu-based catalysts from four crucial steps in CO_2RR-to-C_{2+}:

1. Inhibition of HER. Modification with organic molecules on Cu-

based electrodes surface enhances the hydrophobicity for inhibiting HER. Another way for this goal is designing specific morphology of nanoneedle shape and hydrophobic porous structure for reducing the surface wettability.

2. CO_2 adsorption and activation. Cu-based catalysts supported by CO_2-capture materials can potentially form a local microenvironment with high CO_2 concentration. While, introducing halide ions can donate lone-electron pairs to the unoccupied orbital of CO_2 to facilitate its activation through the formation of the $CO_2^{\bullet-}$ radical. In addition, synergistic effect between $Cu^{\delta+}$ and Cu^0 in Cu surfaces is also efficient to activate CO_2.
3. CO formation and adsorption. The effective methods include addition of foreign component served as CO-generation sites and construction of specific structures with enhanced local electric-thermal fields. They can efficiently modulate the CO coverage, adsorption capacity and adsorption configurations for C–C coupling.
4. C–C coupling. This step can be promoted through constructing confinement structures, adding oxidation states, building defects, designing single-atom catalysts, and constructing heterojunction structures. Cu-based electrode with confinement structure can prolong retention times of intermediates.

Introduction of positive valence Cu sites, defects and heterojunction interfaces mainly modulate the adsorption behaviors of C_1 intermediates and lower the energy barrier of C–C coupling. The ligand groups in single-atom catalysts affect the C–C coupling path between different C_1 intermediates through modulating the coordination micro-environment of Cu sites.

In addition, this work gives insight into the reaction mechanism of CO_2RR by deeply understanding the relationship between surface

properties of Cu-based catalysts and improved performances. Meanwhile, the current challenges and potential strategies of CO_2RR-to-C_{2+} are envisioned. The work was published in *Chinese Journal of Catalysis*.

More information: Huanhuan Yang et al, Efficient strategies for promoting the electrochemical reduction of CO_2 to C_{2+} products over Cu-based catalysts, *Chinese Journal of Catalysis* (2023). DOI: 10.1016/S1872-2067(23)64429-8

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