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COMMENTARY

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Optimizing water activation for efficient CO_2 electroreduction

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Climate change represents one of the most critical global challenges, driving increased focus on the development of sustainable chemical processes. Electrocatalysis has emerged as a highly promising approach for achieving efficient and environmentally benign catalytic processes. Driven by renewable electrical energy, electrocatalysis enables the efficient production of chemicals and fuels from renewable feedstocks with inert bonds under ambient conditions, where water acts as both solvent and proton source. Water activation is essential to generate active hydrogen species (*H) for the hydrogenation step in the electroreduction process; however, excessive activation must be avoided to prevent side reactions, such as the hydrogen evolution reaction (HER), that can detract from the desired catalytic performance.[1] Thus, it is necessary to precise control over the activation of H_2O.

To make full use of *H to improve the efficiency of the reaction, a more in-depth basic knowledge of water activation strategies is needed so that the catalytic system can be rationally designed for optimal performance. In light of this, various heterogeneous catalysts have been designed to optimize the activation of *H, thereby enhancing the overall process. Shao et al. developed a hollow cobalt phosphide nanosphere electrocatalyst integrated onto a self-supported carbon nanosheet array to promote the conversion of NO_3^--to-NH_3 (Figure 1A). This design facilitated a dynamic equilibrium between the generation of active hydrogen on the cobalt phosphide and its consumption by nitrogen intermediates.[2] Han and Sun et al. designed a dual-active site catalyst for CO_2-to-C_2 production, where the atomic Cu sites enhanced H_2O dissociation to generate *H, which then migrated to the Cu nanoparticles, modulating *H coverage and thereby promoting the conversion of *CO to *CHO (Figure 1B).[3] The catalyst achieved a faradaic efficiency (FE) of 75.4% with a partial current density of 289.2 mA cm^{-2} at −0.6 V (versus reversible hydrogen electrode, vs. RHE). Li et al. developed a tandem catalyst composed of Ir single-atom (Ir_1)-doped hybrid Cu_3N/Cu_2O multi-sites achieving a FE of 68.2% for CO_2-to-C_2 production, a high partial current density of 493.1 mA cm^{-2}, and excellent electrochemical stability (Figure 1C).[4] Their proposed reaction pathway highlighted *CO and *CHO as critical intermediates, with the Ir_1 sites in the Ir_1-Cu_3N/Cu_2O catalyst playing a crucial role in enhancing H_2O activation and facilitating *CO protonation, thereby accelerating *CHO formation at the multisite interface.

Electrochemical CO_2 reduction, powered by renewable electricity, offers a promising route for converting abundant and low-cost CO_2 into value-added compounds, contributing to a sustainable, low-carbon future. However, the electrocatalytic reduction of CO_2 to CO is hindered by the energy penalty associated with the hydrogenation step, which results in the formation of the adsorbed *COOH intermediate, slowing down the overall process. Recently, Sun et al. reported a novel strategy for enhancing CO_2RR to CO by designing Ni-partnered heteroatomic dual-atom catalysts (HDACs) with tailored hydrogen adsorption affinities, demonstrating their application in efficient and stable electrochemical CO_2 reduction.[5] The HDACs exhibited exceptional catalytic activity and selectivity, significantly surpassing single-atom electrocatalysts and many previously reported counterparts. Accelerating the generation and transfer of *H to CO_2 molecules would be an effective way to improve the reaction kinetics to form the carbonyl intermediate. The authors initially investigated the adsorption strength of *H on M sites through density functional theory (DFT) calculations. They followed the order: Cd > Pt > Pd. $NiCdN_6$ with *H facilitates optimal adsorption of reaction intermediates and significantly enhances the kinetics of *COOH formation. This behavior differs from the findings reported in previous studies (Figure 1D). Furthermore, they employed a coordination-thermal decomposition method and successfully synthesized the NiCd-HDAC catalyst by atomic capturing.

The NiCd-HDAC catalyst was applied in the electrocatalytic reduction of CO_2 to CO, and exhibited a superior FE_{CO} of ~ 97.1 ± 0.2% at −0.75 V (vs. RHE) and much higher turnover frequency (TOF) value (around 9000 h^{-1}) than both Ni-SAC and Cd-SAC. NiCd-HDAC also exhibited excellent catalytic stability, with minimal current decay and nearly unchanged FE_{CO} even after 55 hours of continuous electrolysis.

To further investigate the reaction mechanism on the catalyst surface, Sun et al. adjusted the proton concentration in the cathode electrolyte by the addition of 0.1 M H_2SO_4 solution. These results indicated that Cd facilitated the generation of *H. Subsequently, they confirmed the above conclusion through *in situ* electron paramagnetic resonance (EPR) spectroscopy using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a radical scavenger, suggesting that the H• formation on NiCd-HDAC was attributed to Cd. The appearance of an EPR signal for •COOH indicated that •H can effectively activate CO_2 to generate •COOH. These results strongly supported the pivotal role of H• in CO_2 reduction. They concluded that the Ni site primarily adsorbed •COOH, while the Cd site mainly activated hydrogen from water. The combined effect of both sites improved the conversion of CO_2 to CO.

Additionally, operando attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) was employed to

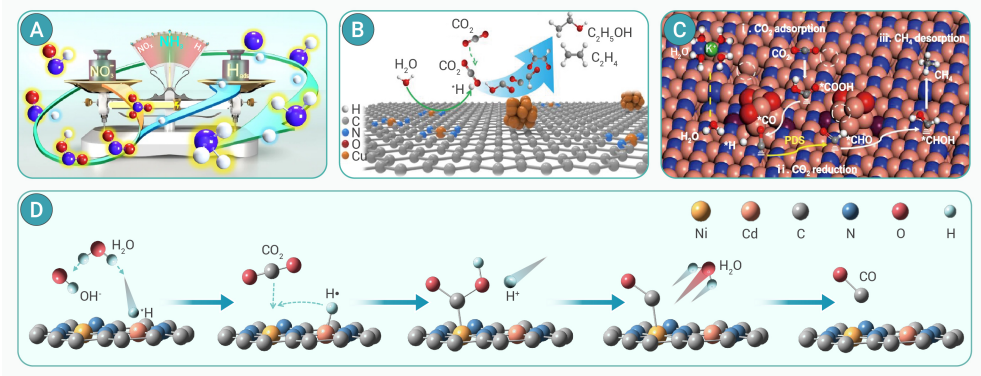

Figure 1. Scheme of the mechanism of *H application in different fields (A) H_{ads} equilibrium boosts NO_3^- reduction to NH_3.Color code: Co light blue, P pink, H white, O red, N dark blue. Source data are provided as a Source Data file. (Adapted with permission.[2] Copyright 2022, Springer Nature.) (B) Proposed reaction mechanism for CO_2RR to C_2 products on the M-Cu_1/CuNP. (Adapted with permission.[3] Copyright 2023, Springer Nature.) (C) Proposed reaction mechanism for the CO_2RR to CH_4 on Ir_1-Cu_3N/Cu_2O.The hollow white circles represent N or O vacancies. Green, K; brick red, Cu; purple, Ir; blue, N; red, O; gray, C; and white, H. (D) Scheme of the *H transfer mechanism. (Adapted with permission.[4] Copyright 2023, American Chemical Society.)

investigate potential reaction intermediates during the electrochemical CO_2 reduction process. Upon switching from CO_2 to CO, the linear adsorption of *CO (*CO_L) peak gradually increased and exhibited a blue shift, reaching near equilibrium after several SEIRAS scans, indicating an increase in the surface coverage of *CO. The lower wavenumber peaks arise from the combined contributions of bridge–bonded CO (*CO_B) and *COOH. The initial decrease in peak intensity was likely due to the gradual transformation and desorption of *COOH. Upon switching the atmosphere back from CO to CO_2, the *CO_L peak in the higher wavenumber range weakened and redshifted, attributing to a decrease in *CO_L surface coverage and a reduction in dipole–dipole interactions. Conversely, the intensity of the peaks in the lower wavenumber range increased, suggesting that CO_2 was initially reduced to *COOH, which accumulated on the surface, thereby enhancing the peak intensity relative to the pre–switch *CO_B coverage. Although the peak positions shift with changes in surface composition and coverage, making it challenging to fully deconvolute the spectra, these results provided an evidence for the formation of *COOH and *CO intermediates (*CO_L and *CO_B).

The method of designing optimal M–sites and tuning the hydrogen adsorption strength, a higher production of *H can be achieved, significantly improving the catalyst's reaction kinetics. The reaction mechanism and catalyst design strategy proposed by Sun et al. provided a promising approach for developing electrocatalysts with high activity and selectivity for CO_2–to–CO conversion. Based on the concepts discussed in this article, the efficiency of copper–based catalysts for producing C_{2+} products can be improved by modifying their structure, which alters how they activate water and enhances their overall performance. Furthermore, this strategy can be applied in other potential areas for electroreduction of various chemicals with inert bonds such as nitric oxide reduction reaction, nitrate reduction (NO_3^-), nitrite reduction (NO_2^-), nitrogen reduction (N_2), CO reduction, and the co–reduction of CO_2/CO and N_2/NO_3^-.

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DECLARATION OF INTERESTS

The authors declare no competing interests.