Dual-Atom Catalyst for Selective CO_2 Reduction

A dual-atom NiCu catalyst achieves record-high selectivity for CO_2-to-ethanol conversion.

The electrochemical reduction of carbon dioxide (CO_2) into valuable multi-carbon fuels is a promising strategy for mitigating CO_2 emissions while producing sustainable chemical feedstocks.[1] However, achieving high selectivity and efficiency for ethanol production remains a major challenge because of the difficulty of C–C coupling and the competitive formation of C1 products. Copper-based catalysts have demonstrated the potential for facilitating C–C coupling, but their selectivity for ethanol is often low, requiring significant overpotentials.[1,2]

To address these challenges, the teams led by Bing Joe Hwang (National Taiwan University of Science and Technology, NTUST), Wei-Nien Su (NTUST), and Meng-Che Tsai (National University of Tainan) demonstrated a dual single-atom catalyst (SAC) system featuring atomically dispersed Ni and Cu sites (NiCu-SACs/N-C), which synergistically enhance ethanol selectivity and catalytic efficiency. **Figure 1(a)** illustrates the rational design and synthesis of NiCu-SACs/N-C prepared *via* hydrothermally assisted pyrolysis using zeolitic imidazolate frameworks.

The synthetic strategy ensures the atomic dispersion of Ni and Cu in a nitrogen-doped carbon matrix, creating abundant accessible active sites. To further elucidate the role of cooperative dual active sites, control experiments in CO-saturated electrolytes were conducted. The results confirm that Ni sites generate labile CO intermediates, which diffuse to adjacent Cu sites for C–C coupling, thereby forming ethanol. A key highlight of this work is the use of Ni–Cu cooperative heteroactive sites, which uniquely facilitate CO_2 reduction to ethanol with an unprecedented Faradaic efficiency (FE) of 92.2% at −0.6 V vs. reversible hydrogen electrode (RHE) (**Fig. 1(b)**). To the authors' knowledge, this represents the highest selectivity reported to date for direct electrochemical CO_2-to-ethanol conversion. The dual-atom catalyst also exhibits the lowest onset potential for ethanol production at −0.4 V vs. RHE, surpassing the performance of single-atom Cu or Ni catalysts. This exceptional performance is attributed to the cooperative entanglement of adjacent Ni and Cu sites, where CO generated on Ni–N_3 sites is efficiently transferred to Cu–N_4 sites for C–C coupling, ultimately leading to ethanol formation.

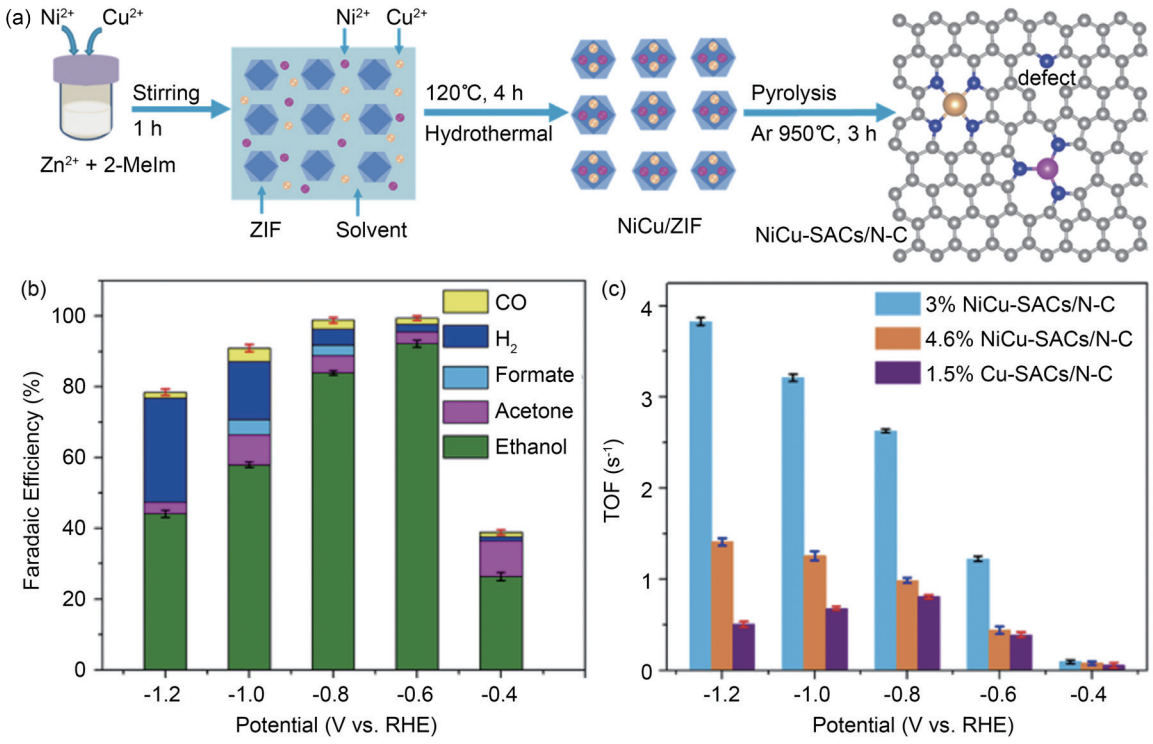

Fig. 1: (a) Schematic representation of the synthesis of dual SACs *via* hydrothermally assisted pyrolysis method. (b) FEs and product distributions over the catalysts of 3% NiCu-SACs/N-C electrodes at different potentials. Error bars indicate the standard deviation. (c) TOF of ethanol over NiCu-SACs/N-C hybrids with different metal loadings, compared with Cu-SACs/N-C at different applied potentials. [Reproduced from Ref. 3]

Figure 1(c) highlights the turnover frequency (TOF) of CO_2-to-ethanol conversion, with the NiCu-SACs/N-C catalyst exhibiting a TOF four times higher than single-atom Cu catalysts. The cooperative synergy between Ni and Cu is also evident in the significantly enhanced electrochemical active surface area and reduced charge transfer resistance (R_{ct}), indicating more efficient electron and mass transport. The computational modeling further supports the experimental findings by demonstrating that the energetically favorable C–C coupling step occurs at the Cu–N_4 sites, which are enhanced by neighboring Ni–N_3 sites. At greater negative potentials, the formation of Cu clusters increases the energy barrier for C–C coupling, leading to a decline in ethanol selectivity. This mechanistic insight explains the volcano-shaped ethanol FE trend observed in the electrochemical studies.

The role of *in situ* X-ray absorption spectroscopy (XAS) is crucial in unraveling the mechanistic insights of this dual-site catalyst. **Figure 2** presents *in situ* extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) analyses. The results reveal a key structural transformation during CO_2 reduction. Notably, while Ni remains in its single-atom Ni–N_3 coordination environment throughout the reaction, Cu undergoes dynamic restructuring, forming potential-induced Cu clusters at high negative potentials. These dynamic Cu clusters play a critical role in modulating catalytic activity, but excessive clustering leads to decreased ethanol selectivity. This observation, which is supported by density functional theory (DFT) calculations, confirms that C–C coupling occurs preferentially on atomically dispersed Cu–N_4 sites rather than Cu clusters, explaining the decline in ethanol FE at highly negative potentials.

In summary, this study establishes NiCu-SACs/N-C as a groundbreaking dual-site catalyst for CO_2-to-ethanol conversion, achieving record-high FE and low onset potential. The findings underscore the importance of cooperative single-atom site engineering and the synergistic role of Ni and Cu in promoting selective C–C coupling. The insights gained from *operando* XAS at **TPS 44A**, electrochemical analysis, and DFT modeling pave the way for designing next-generation electrocatalysts for carbon-neutral fuel production. This work provides a scalable and sustainable strategy for high-selectivity electrochemical CO_2 conversion, contributing to advancements in renewable energy and carbon capture technologies. (Reported by Hao Ming Chen, National Taiwan University)

This report features the work of Bing Joe Hwang, Wei-Nien Su and Meng-Che Tsai published in Appl. Catal. B-Environ. ***358****, 124420 (2024).*

TPS 44A Quick-scanning X-ray Absorption Spectroscopy

- *In situ* XAS
- Materials Science, Electrocatalyst

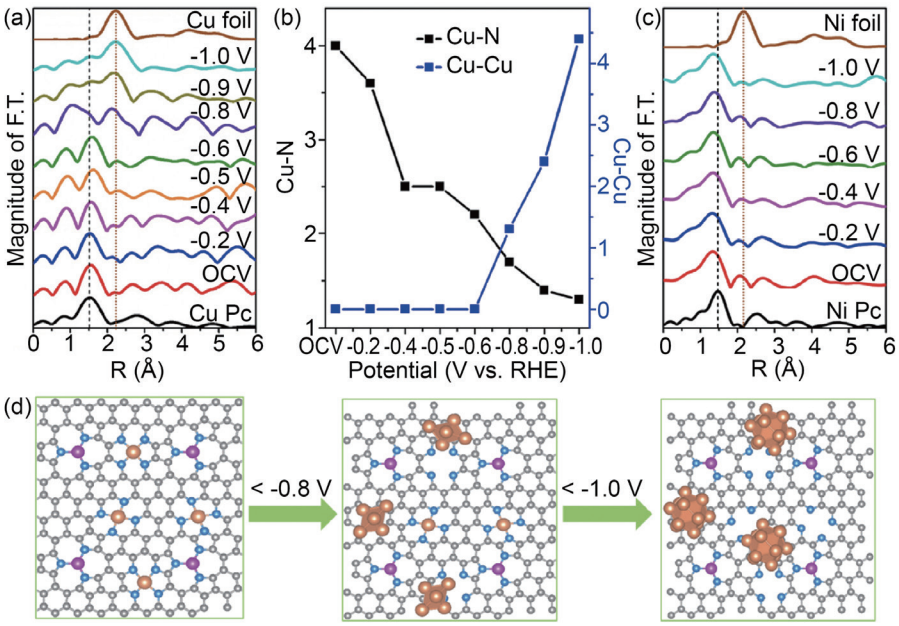

Fig. 2: (a) *In situ* EXAFS spectra and (b) the corresponding average coordination number for Cu–N and Cu–Cu shells of the Cu K-edge for 3% NiCu-SACs/N-C hybrid recorded during the CO_2 electrolysis at different applied potentials in CO_2-saturated 0.5 M $KHCO_3$. Data for CuPc and Cu foil are included for reference. (c) *In operando* EXAFS spectra of Ni K-edge for 3% NiCu-SACs/N-C hybrid recorded during the CO_2 electrolysis at different applied voltages. Data for NiPc and Ni foil are included for reference. (d) The structural models of atomically distributed Ni and Cu sites, as well as the potential-induced dynamic Cu clusters from Cu single atoms, as suggested by *in operando* analysis during the CO_2 electrolysis. [Reproduced from Ref. 3]

References

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