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Reengineering the old wingmen: increasing K^+ coverage to boost electrocatalytic CO_2RR on Cu

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Despite extensive research into combating green-house gas emissions, electrocatalytic CO_2 reduction remains plagued by meagre rates and C_1 product formation. In the recent issue of *Cell Reports Physical Science*, Fan *et al.* report on a catalyst modification using a synergy effect of K^+ to form multi-carbon products on copper.

A mere two centuries ago, fossil fuels were emerging as the energy source of the future. While early civilizations had been puzzled by natural gas and attributed supernatural origins and abilities to it, the early 19th century saw a wide-spread commercialization of natural gas and coal, followed by petroleum. With the development of more efficient engines, advent of catalytic converters and better scrubbing and cleaning systems, fossil fuels appeared to be the energy source of the future.

However, the build-up of the unassuming by-product has quietly ticked up. Since the Industrial Revolution, atmospheric CO_2 concentrations have increased from a stable 280 ppm over the previous 6000 years to more than 420 ppm. As early as 1986, Swedish chemist Svante Arrhenius predicted that rising CO_2 levels could effect global climate change. The first warning articles in public media appeared in the 1930s, and as early as 1988, *The New York Times* ran the headline that global warming had begun. Yet the problem was not recognised for many years and it remains unsolved. CO_2 levels have continued to rise ever since.

In recent decades, it has become clear that reducing energy consumption and transitioning to carbon-free sources alone cannot remedy the situation. On the one hand, their contribution is far too small and does little to reduce CO_2 concentrations. On the other hand, hydrocarbon-based fuels are currently irreplaceable where mass or high exhaust speeds are crucial, such as in aviation. Hence, ways are being sought to *convert* CO_2 into high energy carbon compounds, preferably hydrocarbons. The seminal Fischer-Tropsch process, discovered in the 1920s, has proved how CO can be thermocatalytically converted to liquid hydrocarbons using hydrogen.

Unfortunately, CO₂ does not lend itself to easy reduction due to its remarkably strong C=O bonds. Electrochemical reduction of CO₂ dates back to the late 19th century when CO₂ was reduced to CO on a zinc cathode, while by the 1950s other carbon-containing compounds were already produced.¹ Research in modern CO₂RR gained momentum in the 1980s following the oil crises of the 1970s and growing awareness of rising CO₂ levels. Despite several available methods for CO₂ recycling, including reverse-water gas shift, methanation, Fischer-Tropsch, methanol synthesis and CO₂ fixation, CO₂RR remains the only viable process that can be run at near-ambient conditions and at scale,² although photocatalytic CO₂ reduction is also being investigated.³

Since the seminal 1985 study by Yoshio Hori and co-workers⁴, who achieved a 100 % Faradaic efficiency using a KHCO₃ solution and various polycrystalline electrodes, copper has been recognised as the only metal to non-negligibly and consistently produce multi-carbon species. All other metals produce either formate, CO or hydrogen. However, the ratio of products on copper electrodes can vary drastically with the overpotential, current, catalyst formulation and solution. Several approaches have been proposed to increase the reaction rate and tilt the product distribution to more value-added compounds: testing various Cu(hkl) surfaces or crystal orientations, catalyst pretreatment, restructuring, doping and alloying, probing bimetallics, applying different potentials, using electrolytes and ion effects, electrochemical conditions (temperature, pressure), cell design and employing nanostructures.²

In this issue of *Cell Reports Physical Science*, Zhanxi Fan and co-workers show how potassium cations adsorb more readily to Cu nanosheets and boost the selectivity and productivity of the reaction (Figure 1).⁵ The beneficial effect of potassium cations is by no means surprising, having been observed by Hori as early as 1985. Since the 1990s, it has been known that the selectivity is strongly influenced by the size of the participating cations.⁶ However, the exact explanation of this effect remains elusive due to the complexity inherent in treating the interfaces. Several explanations have been put forward, ranging from nonspecific interactions and specific adsorption, local pH change to promoter-like stabilization of certain intermediates due to electrostatic field stabilization⁷ and electrochemical double layer fine-tuning.⁸ While the mechanism of potassium-induced selectivity enhancement remains an open theoretical question, Fan tackled the problem of increasing the density of adsorbed K⁺.

Fan's group decided to focus on cation engineering, which has recently been recognised as a promising approach to boost the catalyst performance in CO₂RR. They argued that cations, which are known to interact with intermediates and electrolytes, could also affect catalyst surface activity by altering their electronic structure.

The catalyst was prepared experimentally by oxidation and subsequent reduction of copper foils. They were immersed at 60 °C in an aqueous solution of K₂S₂O₈ and NaOH, which oxidised copper. The formation of CuO in the form of nanosheets was indicated by the formation of a black film with an average thickness of 28 nm. This was followed by electroreduction at -0.8 V, which saw the sample turn red as copper nanosheet arrays formed. The metallicity of copper was confirmed by cyclic voltammetry and X-ray diffraction. The thickness of the nanosheets reached about 24 nm but the surface became uneven and varied (Figure 1).

Testing the copper foil and copper nanosheets in a gas-tight H-type cell under ambient conditions revealed a marked difference in their performance. Depending on the applied

potential, the Cu foils produced CO and HCOOH between -0.6 eV and -0.8 eV, and CH₄ at -1.2 V. In contrast, the Cu nanosheets performed differently, exhibited a volcano-like behaviour for CH₄ selectivity and produced mostly C₂₊ products at lower potentials, reaching a ratio C₂₊/C₁ of 7.2 : 1 at 1.1 V, which is 18 times more than Cu foils. As long as the Cu nanosheets were stable, the high ratio persisted and was only affected by the degradation of the nanosheet structure after a few hours (Figure 2).

Assuming that the superior activity of the nanosheets can be traced back to the cation-catalyst effect, the density of adsorbed K⁺ ions was measured using inductively coupled plasma optical emission spectrometry. While it was 0.80 μmol/cm² for Cu foils, it reached 11.7 μmol/cm² for the nanosheets. On the other hand, OH- adsorption proved to be miniscule. Further experimental confirmation was obtained by studying additional electrolytes: LiHCO₃, NaHCO₃, CsHCO₃. As expected, Li⁺ favoured the production of H₂, Na²⁺ produced moderate amounts of C₂₊ species and Cs⁺ excelled at forming higher alcohols (C₂H₅OH and *n*-C₃H₇OH), reaffirming the established cation series effect (Figure 3).

To theoretically demonstrate the beneficial effect of K⁺ as the reason for superior performance of the Cu nanosheets, density functional theory calculations were performed. It was shown that the *d*-band centre in the Cu foil is higher than in the nanosheets, which can cause CO overbinding and shuts down the C₂₊ pathway. Adsorption of K⁺ first decreases the *d*-band centre and then after the inflection point *increases* it, further preventing CO overbinding. PDOS (partial density of states) analyses of crucial intermediates showed that the formation of OCCO is favoured on the nanosheets, while the Cu foil forms mostly CHO and CO, leading up to C₁ products (Figure 4).

To sum up, Fan's group has shown that Cu nanosheets can be prepared easily from Cu foils. Due to their different electrochemical properties, they are more conducive to binding K⁺ cations, which modify the surface to shift the product distribution during CO₂RR towards C₂₊ hydrocarbons. While the beneficial effect of K⁺ has long been known, Fan *et al.* have shown *how* it can be magnified and *why*. These advances show a promising path to further improving CO₂RR, which may only help us get rid of the atmospheric CO₂ but also convert it into the more desired products that can be used in the chemical industry as a precursor, as a reactant⁹ or as carbon neutral fuels. Subsequent research will undoubtedly hone in on further improving the selectivity of copper-nanosheet-like electrocatalysts and tackle the problem from both the experimental as well as theoretical approach, where multiscale modelling has recently become commonplace.¹⁰

Declaration of interests

The authors declare no competing interests.

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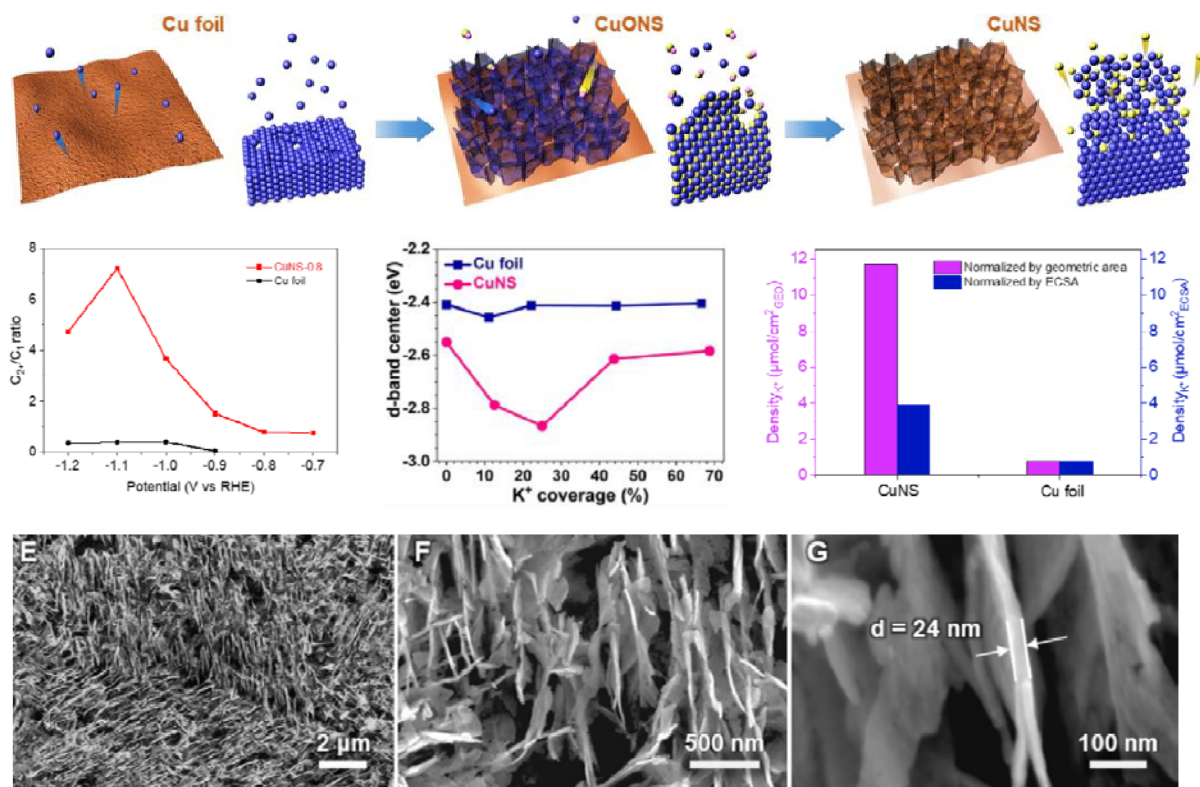


Figure: Top: A schematic illustration of the formation of CuNS. Middle: (left) The C_{2+}/C_1 product ratio, (centre) The dependence of the d -band centre on the K^+ ion coverage, (right) The density of K^+ ions adsorbed on CuNS and Cu foils. Bottom: SEM images of CuNS at different magnifications. Adapted from Ref ⁵.