ELECTROCATALYSIS

Directing CO$_2$ conversion with copper nanoneedles

Selective, electrochemical transformation of carbon dioxide into industrially relevant C$_{2+}$ products has remained a challenge. Now, a copper-based 'nanoneedle' electrocatalyst has been used to selectively convert carbon dioxide to ethylene at extremely high current density.

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Efficiently converting carbon dioxide (CO$_2$) into value-added chemicals and fuels presents an opportunity to reduce the carbon footprint associated with burning fossil fuels. The electrochemical CO$_2$ reduction reaction (CO$_2$RR) is a promising catalytic approach because renewable energy (wind, solar, hydroelectric and so on) can power CO$_2$ conversion electrolysers to produce carbon-neutral products[1,2]. Electrochemical CO$_2$ reduction can also function as an energy-storage platform by converting excess renewable electrons and CO$_2$ into carbon-neutral fuels for later energy production.

Copper is a widely studied CO$_2$RR electrocatalyst because it is one of the few metals that can convert CO$_2$ into hydrocarbons. Unfortunately, copper electrocatalysts often have wide product distributions and undesirable side reactions, including H$_2$ evolution, that may hinder large-scale technological deployment. Selective conversion of CO$_2$ into industrially important C$_{2+}$ species at high current density remains a technical challenge, and controlling structure–selectivity relationships is a central theme for CO$_2$RR electrocatalysis researchers. Writing in *Nature Catalysis*, Sargent and co-workers now report a nanostructured Cu-based electrocatalyst that produces ethylene (C$_2$H$_4$) with impressive selectivity at high current density[3] (Fig. 1). This product has major industrial importance because ethylene is a precursor used for plastics production. In addition to the product's industrial utility, this study clearly demonstrates how catalyst surface structure and copper oxidation state can be used to tune electrocatalyst performance.

The group have previously demonstrated field-induced reagent concentration, which enhances the CO$_2$RR performance of gold nanoneedle electrocatalysts[4,5]. Sharp nanoneedle tips produce large electric fields that concentrate electrolyte cations and CO$_2$ molecules at the catalyst surface. This reagent concentration simultaneously boosts reaction rates while inhibiting competitive
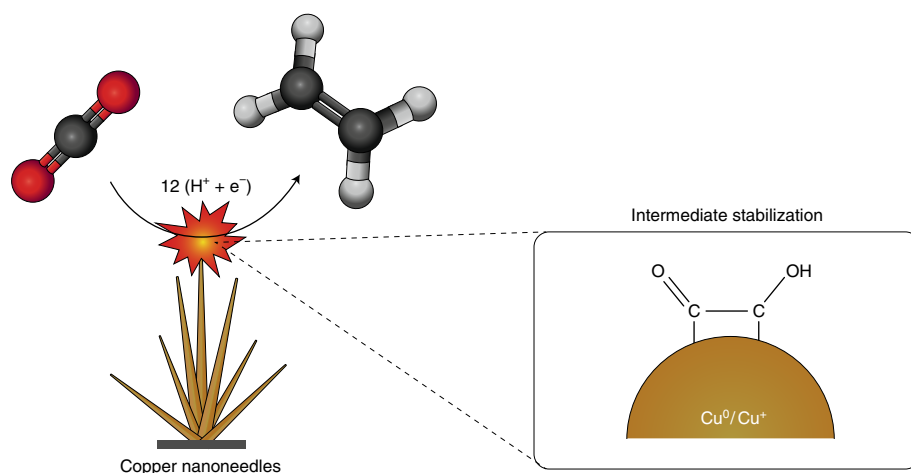

Fig. 1 | Sharp copper oxide nanoneedle electrocatalysts selectively convert carbon dioxide (CO$_2$) and protons into ethylene (C$_2$H$_4$). Large electric fields at the nanoneedle tips concentrate reagents at the catalyst surface and facilitate high current densities. The ability to sustain Cu$^+$ species at negative working potentials improves C$_2$H$_4$ selectivity by stabilizing key reaction intermediates.

H$_2$ evolution at cathodic potentials. This concept has been extended to copper (Cu) oxide materials, and the authors utilized an electro-redeposition technique to electrochemically synthesize highly active Cu oxide nanoneedle structures from a copper oxychloride (Cu$_2$(OH)$_3$Cl) sol–gel precursor. Simultaneous dissolution and redeposition of copper ions during the application of cathodic potentials restructured the sol–gel and created sharp, needle-like Cu oxide nanostructures.

Faradaic efficiency (FE) quantifies the fraction of electrons consumed during the formation of specific CO$_2$RR products. The electro-redeposited Cu oxide electrocatalysts showed an impressive 52% FE for C$_{2+}$ products at −1.2 V versus reversible hydrogen electrode (RHE). C$_2$H$_4$ was the major product (40% FE), alongside H$_2$ (~30% FE) and liquid products (formate, ~18% FE; acetate, ~5% FE; ethanol, ~5% FE). A near complete suppression of gaseous C$_1$ products was achieved, which is important because it could eliminate downstream C$_1$/C$_{2+}$

separation steps and help reduce the complexity of large-scale systems.

The retention of specific surface oxides has been hypothesized to impact CO$_2$RR product selectivity[6,7]. The authors developed an in situ soft X-ray absorption spectroscopy (XAS) technique to monitor the Cu L-edge during electrocatalytic CO$_2$RR. The data indicated retention of Cu$^+$ species at cathodic potentials as large as −1.47 V versus RHE. Time-resolved in situ XAS at −1.2 V versus RHE tracked the reduction kinetics of the catalyst surface. Surface Cu^{2+} species were rapidly reduced to Cu$^+$ within 5 min at relevant CO$_2$RR potentials. However, the reduction of Cu$^+$ to Cu^0 proceeded much more slowly, and the catalyst still retained 23% Cu$^+$ surface species after 1 h of electrolysis at −1.2 V versus RHE. This study provides one of the first examples of the use of in situ Cu L-edge XAS to quantify oxide concentrations in working Cu-based electrocatalysts, and the results provide clear evidence that Cu$^+$ surface species can direct CO$_2$RR selectivity towards C$_{2+}$ products.

The CO_2RR proceeds through a bound *CO intermediate[8]. Protonation of *CO can lead to methane formation, whereas *CO–*CO coupling leads to ethylene formation. The large current densities produced by nanoneedle electrocatalysts increase local pH levels by quickly consuming protons at the catalyst surface. The reduced proton availability inhibits *COH formation and CO–CO coupling pathways become favourable. Under these conditions, CH_4 formation is suppressed while C_2H_4 selectivity is increased. The authors provide atomic-scale insights into the observed CO_2RR structure sensitivity by employing computational modelling. In addition to using state-of-the-art, first-principles computational electrochemistry methods[9], developing faithful representations of the active catalyst site is a key requirement. The authors used experimental information about the catalyst structure and composition during CO_2RR to construct periodic models that included both multifaceted structures and considered the influence of Cu^+ species. Within such a computational framework, correlating intermediate adsorption properties with the active site structure has proven to be a successful method for explaining reactivity trends. The computational results predicted that key ethylene formation intermediates (OCCOH*) were better stabilized at Cu^+-containing surfaces. Taken together, the authors contend sharp Cu nanoneedles boost overall reaction rates by concentrating reagents at the catalyst surface, while Cu^+ surface species enhance C_{2+} selectivity by stabilizing key OCCOH* intermediates.

Finally, the authors incorporated the electro-redeposited Cu catalysts into a gas-flow electrolyser to evaluate system performance in a realistic reactor architecture. The electrocatalysts demonstrated a partial ethylene current density of 161 mA cm^{-2} with 36% FE and negligible methane production (<0.2%). This performance is one of the highest ethylene current densities and C_2:C_1 ratios yet reported. The catalyst still shows some competitive H_2 evolution and further system optimization is needed. However, the results demonstrate exciting progress in the design of selective and active electrocatalyst systems for efficient conversion of CO_2 into industrially relevant chemicals. ❒

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