

ELECTROCATALYSIS

Top tandem team

“The tandem approach will inspire the development of other cooperative systems”

The electroreduction of CO₂ and H₂O into liquid fuels is a promising approach to mitigate CO₂ emissions and meet the rising energy demand. However, the reduction of CO₂ requires an input of energy and a catalyst to control the rates of formation and distribution of products. Now, reporting in *Nature Catalysis*, Christopher Hahn, Thomas Jaramillo and colleagues introduce a Au on Cu tandem catalyst that has unprecedented activity for the electroreduction of CO₂ into multicarbon alcohols at room temperature and pressure.

To date, Cu is the only catalyst to demonstrate appreciable performance in the electrochemical reduction of CO₂ to hydrocarbons and alcohols containing two or more carbon atoms (C₂₊). This conversion is achieved in a multi-step process: CO₂ is first reduced to CO, and this intermediate is then reduced to predominantly hydrocarbons in

subsequent reaction steps. “A major challenge in our search for materials more active than Cu has been discovering a single material with optimal catalytic properties for each and every one of the reaction steps,” states Etosha Cave, a first author of the study. However, the team opened up the search to include bimetallic species composed of Au and Cu, and revealed that the performance of a bimetallic catalyst can be superior to that of the constituent materials. “Coupling Cu to Au, which is the most active metal for the first step of the reaction, relaxes constraints and enables Cu to focus on the downstream reaction steps,” explains co-first author Carlos Morales-Guio.

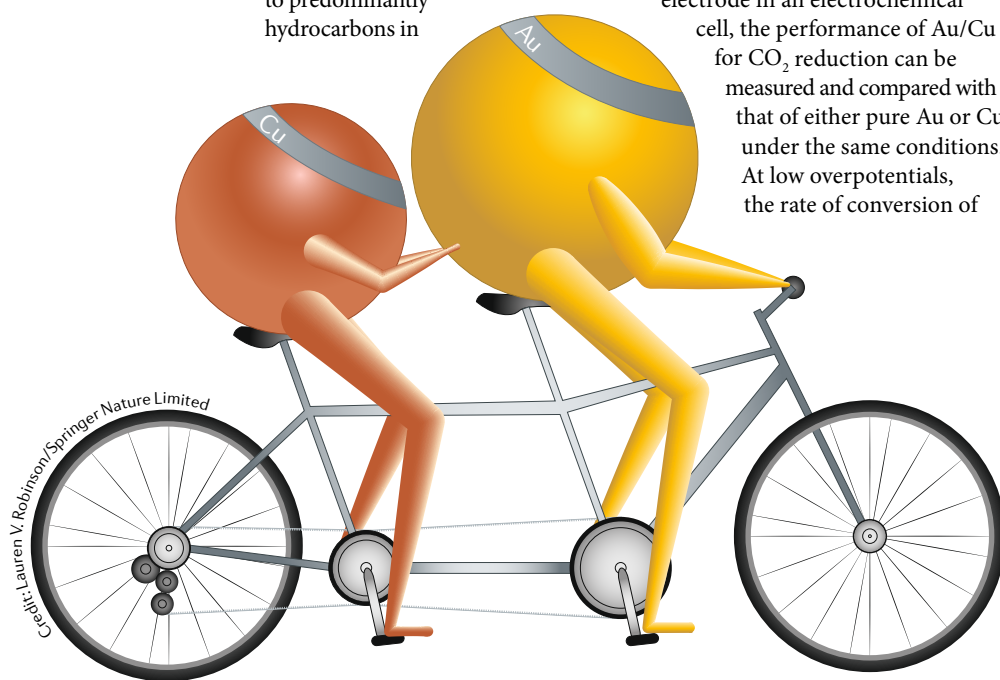
Electron-beam deposition is used to deposit Au nanoparticles onto a polycrystalline Cu film to prepare the bimetallic Au/Cu electrocatalyst. With Au/Cu as the working electrode in an electrochemical cell, the performance of Au/Cu for CO₂ reduction can be measured and compared with that of either pure Au or Cu under the same conditions. At low overpotentials, the rate of conversion of

CO₂ into products more reduced than CO is >100 times faster on Au/Cu than on Cu. Furthermore, unlike either Cu or Au, at low overpotentials, Au/Cu favours the production of C₂₊ alcohols, which are more desirable than hydrocarbons owing to their higher energy density. “The bimetallic electrocatalyst shows synergistic activity, lowering the overpotential required to generate alcohols from CO₂,” summarizes Hahn.

The researchers propose a tandem catalysis mechanism for the reduction of CO₂ on Au/Cu. In the initial step, CO₂ is reduced to CO on the Au nanoparticles, generating a high local concentration of CO. This CO then ‘spills over’ onto Cu, where it is further reduced. Moreover, the team demonstrate that the nanoscale morphology and composition of the bimetallic catalyst is crucial in determining the product selectivity. For example, a AuCu alloy suppressed alcohol formation, indicating that physical separation of Au and Cu is required to achieve selectivity for alcohols.

The team are exploring strategies to further increase the reaction rate, such as integrating Au nanoparticles onto high-surface-area Cu electrodes and the possibility of incorporating bimetallic Au/Cu catalysts into vapour-fed reactors. “The tandem approach will inspire the development of other cooperative systems in which the active sites for sequential reaction steps are separated, allowing for unique catalytic behaviour,” adds Jaramillo.

Claire Ashworth



Credit: Lauren V. Robinson/Springer Nature Limited

ORIGINAL ARTICLE Morales-Guio, C.G. et al. Improved CO₂ reduction activity towards C₂₊ alcohols on a tandem gold on copper electrocatalyst. *Nat. Catalysis* **1**, 764–771 (2018)