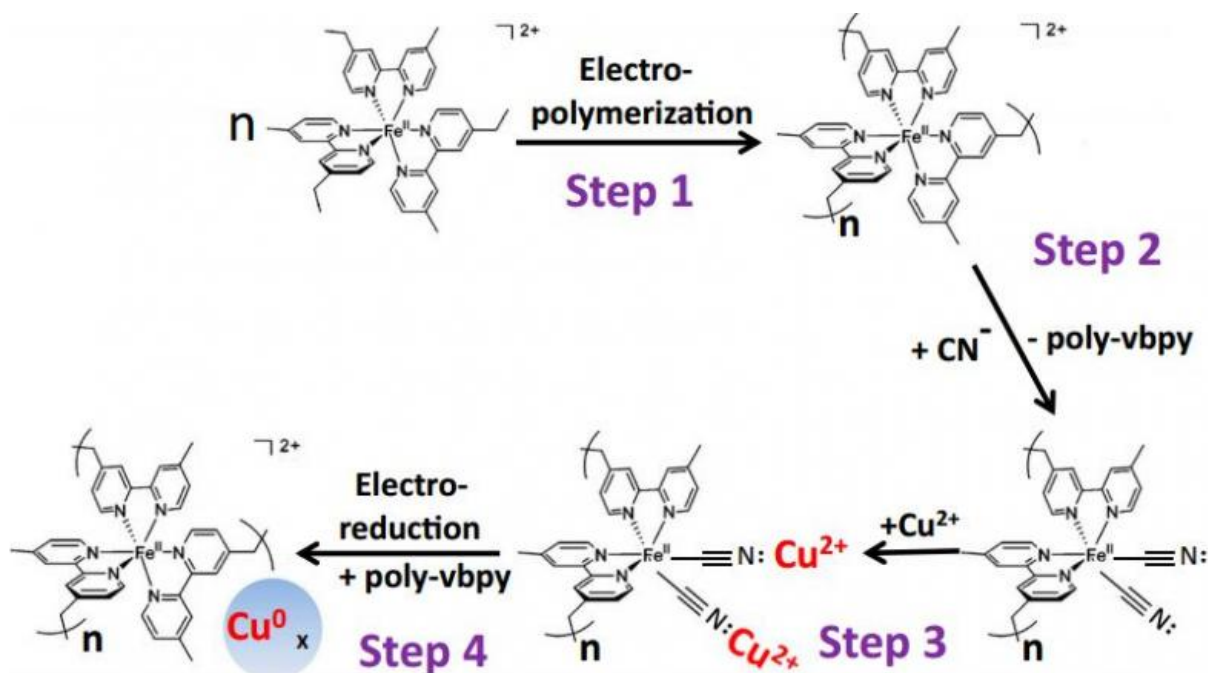


New way to make a CuPd catalyst for the electrochemical reduction of carbon dioxide to methane

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Stepwise synthesis of nanoCu. Step 1: A polymeric film of poly-Fe(vbpy)₃(PF₆)₂ is preformed by reductive electropolymerization. Step 2: Cyanide displacement of a vbpy ligand gives the dicyano film poly-[Fe(vbpy)₂(CN)₂, poly-vbpy]. Step 3: Metal ions Cu(II) are incorporated by binding to the cyanide ligands. Step 4: The bound metal ions are electrochemically reduced to metal nanoparticles. Credit: (c) *Proceedings of the National Academy of Sciences* (2015). DOI: 10.1073/pnas.1522496112

(Phys.org)—A group of researchers from the University of North Carolina in Chapel Hill have devised a generalizable technique for making copper nanoparticles that are of a uniform size and dispersion on a polymeric thin film for the electrocatalytic reduction of carbon dioxide. Their technique involves the electrodeposition of copper and/or palladium metal onto a thin film polymer via coordination of the metal to a cyanide-based ligand complex. Their work appears in the *Proceedings of the National Academy of Sciences*.

Because [carbon dioxide](#) is a greenhouse gas, researchers are interested in ways to decrease the amount of CO₂ in our atmosphere. One feasible solution is to capture CO₂ and reduce it to energy-rich hydrocarbon compounds. However, this needs to be done using methods that do not involve burning more fossil fuels for energy.

One method is to reduce CO₂ using electrocatalysis. This involves using a metal catalyst within an electrochemical cell. Copper has been shown to be a good catalyst for the electrochemical reduction of CO₂. However, there are some problems with using copper foils and crystals including low surface area, low catalytic current densities, and deactivation due to surface buildup. Copper nanoparticles have proved more desirable for these reactions, but their formation typically involves using surfactants, which are difficult to remove and often results in contamination.

Sheng Zhang, Peng Kang, Mohammed Bakir, Alexander M. Lapides, Christopher J. Dares, and Thomas J. Meyer, in their recent paper, demonstrate a technique in which they can produce copper nanoparticles that are the same size and evenly dispersed on a thin film on an electrode. This precludes the needs for a surfactant and allows for smaller particles, which has better catalytic efficiency.

The thin film used is poly-[Fe(vbpy)₃][PF₆]₂ which is then treated with TBAPF₆/CH₃CN such that cyanide ions replace one of the bipyridine

groups. These two cyanide groups, once part of the iron complex, serve as ligands for Cu(II). Electrochemical reduction of Cu(II) produces an ultrafine film of Cu(0) nanoparticles on the polymer surface.

Zhang, et al. tested the generalizability of their technique using palladium to make palladium nanoparticles and CuPd nanoalloys. In testing their catalysts, CuPd had the highest Faradaic efficiency for the reduction of CO₂. Furthermore, studies showed that in this reaction both CO and CH₄ were present.

Electrocatalytic activity was tested using a glassy carbon electrode and controlled potential electrolysis in CO₂-saturated solutions of 0.1 M TBAPF₆/CH₃CN solution with 1M added H₂O. Products in solution were analyzed using ¹H NMR and products in the headspace were analyzed using gas chromatography. Products were CO, CH₄, and H₂, with CuPd nanoalloy producing the highest Faradaic efficiency for CH₄. Additional studies on how alloy composition affects Faradaic efficiency showed that maximum yield for methane was Cu₂Pd.

The formation of CH₄ is important because this allows for a longer lifetime for the electrode. CO results in degradation and carbon deposition. The formation of methane keeps this from happening so quickly. Zhang, et al. speculate that the reason why the nanoalloy does so well for forming methane has to do with a palladium hydride reduction of CO. Electrochemical studies without the hydride reaction indicate that methane production is tied to Pd-H formation.

This technique involving the formation of metal or metal alloy nanoparticles on a thin film using coordination chemistry is a good step in finding ways to reduce carbon dioxide and form high energy carbon products that is environmentally safe and does not involve the use of contaminants.

More information: Sheng Zhang et al. Polymer-supported CuPd nanoalloy as a synergistic catalyst for electrocatalytic reduction of carbon dioxide to methane, *Proceedings of the National Academy of Sciences* (2015). [DOI: 10.1073/pnas.1522496112](https://doi.org/10.1073/pnas.1522496112)

Abstract

Developing sustainable energy strategies based on CO₂ reduction is an increasingly important issue given the world's continued reliance on hydrocarbon fuels and the rise in CO₂ concentrations in the atmosphere. An important option is electrochemical or photoelectrochemical CO₂ reduction to carbon fuels. We describe here an electrodeposition strategy for preparing highly dispersed, ultrafine metal nanoparticle catalysts on an electroactive polymeric film including nanoalloys of Cu and Pd. Compared with nanoCu catalysts, which are state-of-the-art catalysts for CO₂ reduction to hydrocarbons, the bimetallic CuPd nanoalloy catalyst exhibits a greater than twofold enhancement in Faradaic efficiency for CO₂ reduction to methane. The origin of the enhancement is suggested to arise from a synergistic reactivity interplay between Pd–H sites and Cu–CO sites during electrochemical CO₂ reduction. The polymer substrate also appears to provide a basis for the local concentration of CO₂ resulting in the enhancement of catalytic current densities by threefold. The procedure for preparation of the nanoalloy catalyst is straightforward and appears to be generally applicable to the preparation of catalytic electrodes for incorporation into electrolysis devices.

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