Polymer-supported CuPd nanoalloy as a synergistic catalyst for electrocatalytic reduction of carbon dioxide to methane

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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.

solar energy | carbon dioxide reduction | CuPd nanoalloy | electropolymerized film | hydrocarbon

Developing sustainable energy resources and strategies to combat the hazards associated with the use of fossil fuels, which include global warming due to the increased concentration of greenhouse gases, is an important theme in the current energy and environmental research agenda (1–3). Electrochemical and photoelectrochemical CO₂ reduction to energy-dense hydrocarbon fuels could play a major role and become part of an integrated energy storage strategy, in combination with solar- or wind-generated electricity, as a way to store energy in the chemical bonds of carbon-based fuels (4–12). Metal-based catalysts for CO₂ reduction have been extensively studied over the last three decades. Metallic copper has proven to be the best available catalytic material for CO₂ reduction to hydrocarbons by electrochemical methods (13–19). Cu foils and single crystals have been extensively investigated but suffer from low surface areas, low catalytic current densities, and rapid deactivation during electrochemical CO₂ reduction (20). Recently, nanoparticle Cu catalysts (nanoCu) have been investigated as a way to increase catalytic current densities and stabilities. However, Faradaic efficiencies for electrocatalytic reduction to hydrocarbons decrease dramatically with particle size falling to ~10% for particles less than 20 nm in diameter. The size effect has been attributed to an enhanced chemisorption strength for CO at small Cu nanoparticles compared with large particles or bulk Cu electrodes (13). An additional complication arises from the use of surfactants in the syntheses of nanoCu because they can lead to significant contamination issues requiring their removal by a high-temperature posttreatment which causes adverse particle growth and loss of monodispersity (21).

Electrodeposition provides a facile and scalable technique for preparing catalytic electrodes. However, it can be difficult to control

and typically leads to large particle sizes, often from hundreds of nanometers to micrometers in diameter (22), resulting in low catalytic surface areas. We describe here a novel electrochemical method for synthesizing ultrafine metal nanoparticles and their application to CO₂ reduction. It is based on the use of an electropolymerized, electroactive film of a vinyl-2,2'-bipyridine complex of Fe(II). Following treatment with cyanide to displace a bpy ligand and coordinate cyanide, the Fe–CN groups provide a basis for binding metal ions from external solutions (21). After reduction of the film-incorporated metal ions to the corresponding metals, migration occurs to film surfaces where nanoparticles form with size control.

An outline for the overall procedure is shown in Fig. 1 for the surface-film-based reduction of Cu(II) to Cu(0). It involves in sequence: (i) Formation of a polymeric film of poly-[Fe(vbpy)₃](PF₆)₂ (vbpy is 4-methyl-4'-vinyl-2,2'-bipyridine) by electropolymerization induced by vbpy-based reduction. The electropolymerization procedure has been applied to polymer film formation on a variety of conductive substrates (23–26) including glassy carbon (GC) electrodes, planar fluorine-doped tin oxide (FTO) slides, reticulated vitreous carbon, and high surface area gas diffusion electrodes. (ii) Addition of cyanide ions which displaces a vbpy ligand from Fe(II) to give poly-Fe(vbpy)₂(CN)₂, poly-vbpy. (iii) Binding of Cu(II) ions from an external solution with coordination to the cyanide ligands. (iv) Electroreduction of the Cu(II) ions to give ultrafine nanoCu of uniform distribution on the surface of the polymeric film.

Significance

Photo- and electrochemical CO₂ reduction to carbon fuels is not only an attractive solution to the greenhouse effect, but could also become an integral part of a global energy storage strategy with renewable electrical energy sources used to store energy in the chemical bonds of carbon fuels. A novel electrodeposition strategy is reported here for the preparation of highly dispersed, ultrafine metal nanoparticles and nanoalloys on an electroactive polymeric film. It is shown that a bimetallic Cu–Pd nanoalloy exhibits a greater than twofold enhancement in Faradaic efficiency for CO₂ reduction to methane compared with a state-of-the-art nanoCu catalyst. The fabrication procedure for the alloy nanoparticles is straightforward and applicable as a general procedure for catalytic electrodes for integrated electrolysis devices.

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Fig. 1. Stepwise synthesis of nanoCu. Step 1: A polymeric film of poly- $[\text{Fe}(\text{vbpy})_3](\text{PF}_6)_2$ is preformed by reductive electropolymerization. Step 2: Cyanide displacement of a vbpy ligand gives the dicyano film poly- $[\text{Fe}(\text{vbpy})_2(\text{CN})_2, \text{poly-vbpy}]$. Step 3: Metal ions $\text{Cu}(\text{II})$ are incorporated by binding to the cyanide ligands. Step 4: The bound metal ions are electrochemically reduced to metal nanoparticles.

The generality of the procedure is also demonstrated with an extension to the synthesis of polymeric films surface-loaded with nanoPd and with bimetallic CuPd nanoalloy. We demonstrate that the Cu-loaded films are electrocatalysts for CO_2 reduction to methane and that, compared with nanoCu, which, to date, is the best catalyst for

CO_2 reduction to hydrocarbons (13), the bimetallic CuPd nanoalloy provides an enhancement in Faradaic efficiency for CO_2 reduction to methane of >2 in both aqueous and organic solutions. The notable reactivity enhancement appears to arise from a synergistic mechanism involving Pd-H reduction of adsorbed CO from CO_2 reduction on Cu.

Fig. 2. (A) Reductive electropolymerization of $[\text{Fe}(\text{vbpy})_3](\text{PF}_6)_2$ on a prepolished GC electrode by repetitive cycles at 100 mV/s between -1 and -2.1 V vs. Ag/AgNO_3 in 0.1 M $\text{TBAPF}_6/\text{CH}_3\text{CN}$ containing 0.5 mM $[\text{Fe}(\text{vbpy})_3](\text{PF}_6)_2$. (B) Peak currents as a function of the number of scans for the electrode in Fig. 1A. (C) CVs of the final electrode at 50 mV/s following 30 cycles between -2.1 and 1 V vs. Ag/AgNO_3 in 0.1 M $\text{TBAPF}_6/\text{CH}_3\text{CN}$. (D) CV of the poly- $[\text{Fe}(\text{vbpy})_3]^{3+/2+}$ couple at 10 mV/s between 0 and 1 V vs. Ag/AgNO_3 in a fresh solution of 0.1 M $\text{TBAPF}_6/\text{CH}_3\text{CN}$.

−1 and −1.6 V vs. Ag/AgNO₃ in 0.1 M TBACN/CH₃CN resulted in the reduction of Cu(II) to Cu(0). Fig. 4A shows typical transmission electron microscope (TEM) images of the resulting nanoCu embedded in the film structure. They are ~7.8 nm in diameter and highly dispersed. Almost all of the Cu nanoparticles (*SI Appendix, Fig. S4*) were exposed on the polymeric film surface, and readily accessible to CO₂ in the electrolyte.

The impact of the CN[−] coordination strategy on particle dimensions was investigated by comparing the products of electrochemical reduction of CN[−] treated polymeric films of poly-[Fe(vbpy)₃](PF₆)₂ in 0.1 M TBAPF₆/CH₃CN on a planar FTO slide with a non-CN[−]-containing film. In the absence of cyanide, large, agglomerated Cu particles are produced (*SI Appendix, Figs. S5 and S6*) in marked contrast to the dispersed, ultrafine nanoparticles obtained when the film is pretreated with CN[−].

In the dicyano films, a coordinated vbpy ligand in a poly-Fe(vbpy)₃(PF₆)₂ site is displaced by two CN[−] ligands followed by Cu(II) binding. Addition of CN[−] with coordination to Fe(II) occurs with high local homogeneity given the metal complex structure and initial reduction is homogeneously dispersed throughout the film structure. Following an initial reductive scan of Cu(II)-bound cyano films, Cu(0) appears and is dispersed throughout the film, initially with a continuing interaction with the cyanide ligands. At longer times Cu(0) aggregates form locally, initially as small Cu nanoclusters which diffuse to the surface of the films with formation of the ultrafine nanoCu (24).

The broader applicability of the cyanide coordination strategy was examined by the analogous synthesis of small, ultrafine nanoPd particles (~4.6 nm, *SI Appendix, Fig. S7*) shown in Fig. 4B and of bimetallic CuPd nanoalloy (~6.6 nm, *SI Appendix, Fig. S8*) in a 1:1 molar ratio (Fig. 4C). Diffraction peaks for bimetallic CuPd

Fig. 4. Typical TEM images of nanoPd (A), nanoCu (B), CuPd nanoalloy (C), and Cu₂Pd nanoalloy (D) on the polymeric film. (E) Plots of Faradaic efficiencies for methane production vs. applied potential on nanoCu, nanoPd, and CuPd nanoalloy. (F) Methane yields (recorded at −1.8 V vs. Ag/AgNO₃) at Cu₃Pd, Cu₂Pd, CuPd, CuPd₂, and CuPd₃ nanoalloy catalysts. CO₂ reduction was performed in CO₂-saturated 0.1 M TBAPF₆/CH₃CN solutions with 1 M added H₂O.

nanocatalyst in *SI Appendix, Fig. S9* can be indexed as (111), (200), (220), and (311) reflections for the fcc structure for the CuPd nanoalloy. For both the Cu- and nanoalloy-containing films, retention of the Fe(II) in the films was shown by UV-visible absorption measurements.

These results suggest that the polymer film/coordination/reduction strategy may provide a general electrochemical procedure for synthesizing ultrafine, monodispersed metal nanoparticles on/imbedded in an electroactive polymer film without the use of surfactants.

Electrocatalytic Reduction of CO₂ to Methane. The electrocatalytic reactivity of the nanoparticle films on a GC electrode toward CO₂ reduction was evaluated by controlled potential electrolysis in CO₂-saturated 0.1 M TBAPF₆/CH₃CN solutions with 1 M added H₂O. The mixed solvent strategy exploits the higher CO₂ solubility in CH₃CN, which is ~eightfold greater than in water (30). The products of CO₂ reduction were analyzed by both ¹H NMR in the liquid phase and by GC in the headspace. Results of the electrolyses at CuPd nanoalloys, nanoCu, and nanoPd are summarized in *SI Appendix, Table S1*. Catalytic currents were stable over extended electrolysis periods as shown in *SI Appendix, Fig. S17*. The products of electrolysis were CH₄, CO, and H₂.

The 8e⁻/8H⁺ product, CH₄, is the most highly reduced product. The ultrafine nanoCu catalyst produced CH₄ with 15% Faradaic yield, which is comparable to previous reports (13). A notably enhanced catalytic reactivity toward reduction to CH₄ is observed for the CuPd nanoalloy. No CH₄ was detected at poly-[Fe(vbpy)₃](PF₆)₂ film under the same conditions. Fig. 4E shows potential-dependent Faradaic efficiencies for CH₄ produced at ultrafine nanoCu, nanoPd, and bimetallic CuPd nanoalloy. The maximum Faradaic efficiency for CH₄ of 33% was achieved for the bimetallic CuPd nanoalloy, a doubling of yield compared with nanoCu. Moreover, the onset for CO₂ reduction to CH₄ at CuPd nanoalloy appears at ~-1.6 V vs. Ag/AgNO₃ (an overpotential of 0.66 V for the CO₂/CH₄ couple; see *SI Appendix, Table S1* for details), which is ~400 mV more positive than at nanoPd and ~200 mV more positive than at nanoCu.

As shown in *SI Appendix, Fig. S17*, compared with carbon black as the electrode substrate (*SI Appendix, Fig. S18*), the polymer-film-supported CuPd nanoalloy exhibited an enhanced current density by a factor of ~3 (~6 mA cm⁻²) compared with nanoCu under the same electrolysis conditions. This may be a consequence of the concentration of the active catalyst on the film surface and of enhanced local concentration of CO₂ in the polymer film (31).

The effect of alloy composition on Faradaic efficiencies for CH₄ production was investigated systematically by use of series of Cu/Pd nanoalloy samples with varying ratios of Cu and Pd from 3:1–1:3. TEM images and size-distribution histograms are shown in *SI Appendix, Figs. S10–S13*. Their reactivities toward CO₂ reduction were first investigated in CO₂-saturated 0.1 M TBAPF₆/CH₃CN solutions with 1 M added H₂O. Methane yields as a function of composition in Fig. 4F show that the maximum Faradaic efficiency (51%) for methane is found to occur for the Cu₂Pd nanoalloy shown in Fig. 4D with a rationale discussed below.

Aqueous CO₂ reduction activities have been also evaluated at the optimal Cu₂Pd nanoalloy and compared with nanoCu as a catalyst in 0.1 M KHCO₃ aqueous solutions by controlled potential electrolysis at -1.68 V vs. SCE. Under these conditions the methane yield is 36% for the Cu₂Pd nanoalloy compared with 13% for the nanoCu catalyst, demonstrating a significant enhancement toward CO₂ reduction to CH₄ in both aqueous and organic solvents with an intrinsically higher reactivity for the nanoalloy. The methane yield was further enhanced to 48% by electrolysis in aqueous solution at 0 °C. The Cu₂Pd nanoalloy catalysts have methane yields that are comparable to bulk Cu electrodes but with significantly enhanced stability toward degradation

in the rate of methane production with time (see *SI Appendix, Fig. S14* for details).

Discussion

To gain mechanistic insight into electrocatalytic CO₂ reduction at the bimetallic catalyst, partial current density Tafel plots for CO₂ reduction to CH₄ at CuPd nanoalloy and nanoCu are compared in *SI Appendix, Fig. S15*. The Tafel slope for CuPd nanoalloy is calculated to be 70 mV dec⁻¹, which is consistent with a mechanism involving a chemical rate-determining step (RDS) (5). In earlier studies on CO₂ reduction to methane at Cu, Hori et al. concluded that the RDS involved an adsorbed CO reaction step (32, 33). Hydride reduction of transition metal bound or free CO is a well-known reaction (34–37). A reasonable suggestion for the appearance of CH₄ on the CuPd nanoalloy is that the rate-limiting Pd–H reduction of adsorbed CO occurs following CO₂ reduction to CO at Cu.

We have explored this reactivity with the electrochemically generated hydride Ru(tpy)(bpy)H⁺ as a homogeneous catalyst. It is generated in situ by electrochemical reduction of Ru(tpy)(bpy)(NCMe)²⁺ in MeCN with added water at potentials more negative than -1.95 V vs. Ag/AgNO₃ as described in our previous report (38). As shown in *SI Appendix, Fig. S16A*, addition of the Ru(II) complex at a nanoCu electrode resulted in catalytic current enhancement. In the differential pulse voltammetry curve in *SI Appendix, Fig. S16B*, reduction peaks at -1.55 V and -1.88 V vs. Ag/AgNO₃ appear due to sequential one-electron reductions at tpy followed by one-electron bpy reduction (38). *SI Appendix, Fig. S16C* shows that, with added complex, the methane yield increases from 6% to 16% at an applied potential of -2 V, conditions known to reduce the nitrile complex to the hydride. Under these conditions, the CO yield decreased from 16% to 8%. Electrolysis at -1.8 V, without reduction to the hydride, results in essentially no change in the methane yield, 4% vs. 3%. These results are consistent with facilitation of methane formation by the electrogenerated hydride, presumably by reduction of surface-bound CO.

Hori et al. reported that during CO₂ electroreduction at Cu foil electrodes, about 90% of the Cu surface area was covered by adsorbed CO from reduction of CO₂ (32). Small Cu nanoparticles have stronger chemisorption binding strengths to CO than large particles or bulk Cu (13) and the surface of the nanoCu catalyst is presumably covered by adsorbed CO, resulting in the very low methane yields (~10%) observed at nanoCu. For the CuPd nanoalloy, Pd-hydride sites generated in situ presumably facilitate the reduction of CO adsorbed at Cu sites to methane. The maximum methane yield is achieved for the Cu₂Pd nanoalloy. Catalysts with a higher Cu ratio, Cu₃Pd, produce more CO, whereas more hydrogen is generated at samples higher in Pd (CuPd, CuPd₂, and CuPd₃).

Relatively high methane yields (over 50%) have been obtained at bulk Cu electrodes but they suffer from severe poisoning and deactivation during CO₂ reduction (20). Deactivation originates from the deposition of heavy metal impurities in the electrolyte and from the formation of graphitic carbon on Cu electrode surfaces (20). Metal impurities in the electrolyte have been removed by preelectrolysis (20), but the formation of graphitic hydrocarbons continues with hydrogen evolution increasing at the expense of CO₂ reduction within an hour after initiation of electrolysis. The change in products is mainly due to the formation of a graphitic carbon layer which prevents CO₂ reduction (39, 40). In contrast, nanostructured Cu catalysts have been found to be stable over 5 h of CO₂ electrolysis, with the increase attributed to the higher surface areas at the nanoparticle catalysts (19, 41). The production rate of methane at the CuPd nanoalloy catalyst remains stable over 3 h of CO₂ electrolysis, which is a notable observation. This catalyst has the dual advantages of relatively high methane yield, comparable to bulk Cu, but with significantly enhanced long-term performance.

We report here a film-based cyanide coordination protocol for templated electrochemical reduction of bound metal ions, Cu(II), Pd(II), which upon reduction, give uniform, ultrafine metal nanoparticles on the surfaces of conductive, electropolymerized films. The procedure, with electroreduction of homogeneously dispersed, chemically bound metal ions, results in the formation of metallic nanoclusters on the film surfaces. It provides what could become a broad, general approach for the synthesis of nanoscale metal and metal alloy particles on electroactive substrates. It is notable that the cyanide-film strategy described here is facile and general and amenable to scale up with the possibility of using of gas diffusion electrodes to achieve high current densities and efficiencies for CO₂ reduction.

Simultaneous coordination of Cu(II) and Pd(II) followed by reduction results in a CuPd nanoalloy with enhanced Faradaic efficiency and a decrease in onset potential for electrocatalytic CO₂ reduction to methane. An optimized Faradaic efficiency for CH₄ production of 51% was obtained at a Cu₂Pd nanoalloy. The

origin of the bimetallic synergistic effect appears to lie in the rate-limiting Pd–H reduction of Cu-bound CO. This finding provides new insights into CO₂ reduction with design and control of product distribution by varying alloy composition and solution conditions. The use of an external, homogeneous cocatalyst for hydride formation and enhanced CO₂ reduction to methane is also a notable observation, one that could presage a general, integrated heterogeneous/homogeneous catalytic strategy for CO₂ reduction and other reactions in the future.

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