CO₂ reduction to acetate in mixtures of ultrasmall (Cu)ₙ(Ag)ₘ bimetallic nanoparticles

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Monodispersed mixtures of 6-nm Cu and Ag nanoparticles were prepared by electrochemical reduction on electrochemically polymerized poly-[Fe(vbpy)]₆(PF₆)₂ film electrodes on glassy carbon. Conversion of the complex to poly-[Fe(vbpy)]₆(cn)₂ followed by surface binding of salts of the cations and electrochemical reduction gave a mixture of chemically distinct clusters on the surface, (Cu)ₙ(Ag)ₘ(polymer/glassy carbon electrode (GCE), as shown by X-ray photoelectron spectroscopy (XPS) measurements. A (Cu)ₙ(35Å)-polymer/[Fe(vbpy)]₆(PF₆)₂(GCE) electrode at −1.33 V vs. reversible hydrogen electrode (RHE) in 0.5 M KHCO₃, with 8 ppm added benzo triazolate (BTA) at 0 °C, gave acetate with a faradaic efficiency of 21.2%.

CO₂ reduction | electrocatalysis | electrodeposition | bimetallic nanoparticles | artificial photosynthesis

Efficient reduction of carbon dioxide to useful fuels and chemicals is an important research goal of artificial photosynthesis (1–7). Solar or electrochemical reduction of CO₂ is complicated by the large overpotentials required for one-electron transfer reduction to CO₂⁻ [with E(CO₂/CO₂⁻) = −1.9 V vs. normal hydrogen electrode (NHE) at pH 7] and a high reorganization energy (8). Subsequent steps to give formate or CO are energetically more favorable. A growing number of catalytic systems for CO₂ reduction have been identified that give C₁ products (9–13) but obtaining multilayer (C₃₄)ₙ products has proven more difficult due to the high barrier for C–C bond formation on electrode surfaces (14).

Current research has led to robust catalysts for CO₂ reduction, including molecular (15, 16), metallic (10, 17, 18), and nonmetallic catalysts (9) with an extensive literature on metal catalysts (19, 20). Cu has proven to be the most effective metal for CO₂ reduction catalyst with an ability to form a variety of high-energy-density products including high-value-added, multiple carbon, Cₓ⁺, products (20). At Cu electrodes, Jaramillo and coworkers (21) have identified 16 CO₂ reduction products, including 12 multicarbon products. In follow-up experiments, the lack of selectivity by Cu has led to the synthesis of Cu-based bimetallic catalysts (3, 22, 23) or to decreases in the size of the Cu catalysts (24). In these experiments, difficulties arise from complicated and time-consuming synthetic procedures by contamination by added surfactants and catalysts (25).

Electrochemical deposition provides a fast and convenient approach for depositing nanoparticles on electrode surfaces (26). The procedure can be less time-consuming than wet chemical synthesis, but there are difficulties in obtaining small, confined nanoparticles and an extended range in size from hundreds of nanometers to micrometers in diameter (27). Here we utilize a procedure described earlier for surface binding and cluster formation (24) to prepare ~6-nm clusters of Cu and Ag on the surfaces of electropolymerized films. We also report that surface-dependent, electrochemical reduction of CO₂ occurs on these surfaces with C–C coupling to give acetate as a significant product.

Results and Discussion

A general procedure for preparation of the electrodes has been described previously (2, 28) and is shown in an adapted form in Scheme 1. The procedure, the vinyl-derivatized salt [Fe(vbpy)]₆[PF₆]₂ (vbpy is 4-methyl-4’-vinyl-2,2’-bipyridine) is electropolymerized on the surface of a glassy carbon electrode (GCE). Subsequent addition of CN⁻ to an external solution causes displacement of a –vbpy ligand by CN⁻ by immersing the polymerized electrode in 0.1 M [TBA][CN] for 20 min (28). The CN⁻ ligands act as a bridge to added cations in solution and exposure of the films gives the ligand-bridged film adducts FeII-CN-M³⁺ (2, 28). Further reduction of the films at potentials sufficient to reduce the coordinated metal ions results in reduction and transfer of the reduced metals to the surface of the films, Eq. 1, where nanoparticles form. For films loaded with multiple metal ions, composite nanoclusters form on the electrode surface providing a basis for multiple surface interactions and cluster formation. On surfaces on which multiple nanoparticles are added, the ratio of available metals can be tuned by the metal ion composition in the precursor solution.

\[ n\text{Fe}^{II}\cdot\text{CN-M}^{m+}, \text{vbpy} \xrightarrow{\text{anod}} \text{CN}^{-} \rightarrow n\text{Fe}^{II}(\text{vbpy})^{2+}\cdot(M)_{x}^{0}. \]  

Polymerization of [Fe(vbpy)]₆³⁺ onto a 0.071 cm² GCE in 1 mM solution, in 0.1 M TBAPF₆ MeCN, was monitored by cyclic voltamogram (CV) scanning at 250 mV s⁻¹ (Fig. L4). Well-defined redox waves for the couples poly-[Fe(vbpy)]₆⁺/⁺⁺ and poly-[Fe(vbpy)]₆⁺/Ⅲ at E₁/₂ = −1.28 V and −1.45 V vs. Ag/Ag⁺ were observed. As shown, the peak currents increase with the number of cycles, consistent with the growth of poly-[Fe(vbpy)]₂⁺ on the electrode surface. The latter occurs by reduction of the

Significance

Efficient reduction of carbon dioxide to useful fuels and chemicals is an important research goal in artificial photosynthesis. Significant progress has been made for the C₁ products, CO and HCOO⁻. We report here a procedure based on the use of ultrasmall, monodispersed Cu and Ag bimetallic nanoparticles on thin, electrochemically polymerized poly-[Fe(vbpy)]₆(PF₆)₂ films. They reduce CO₂ to acetate at pH 7 in aqueous HCO₃⁻ solutions at relatively high efficiencies with significant rate enhancements with added benzo triazolate. In the sequence of clusters, the most efficient results for acetate production were obtained in films of (Cu₃Ag)ₓ with a faradaic efficiency of 21.2% for acetate from CO₂ at −1.33 V vs. reversible hydrogen electrode in 0.5 M KHCO₃ with 8 ppm of added benzo triazolate at 0 °C.

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vbpy ligands to vinyl radicals, initiating C–C bond formation (2, 28, 29). Given the presence of multiple polymerizable vinyl substituents, polymerization is accompanied by extensive cross-linking as the polymer deposits on the electrode surface to form the porous open structure shown in Fig. 1E. The surface coverage of poly-[Fe(vbpy)]$_3^{3+/2+}$ was estimated to be 6.44 ± 0.48 nmol/cm$^2$ from peak current integrations of the poly-[Fe(vbpy)]$_3^{3+/2+}$ wave at $E_{1/2} = 1.03$ V vs. Ag/Ag$^+$(Fig. 1B). Based on this analysis, the coverage used in this study was ∼80 molecular layers with a monolayer surface coverage of 8 × 10$^{-11}$ mol/cm$^2$(2, 28, 29). The thickness of the polymer film on the electrode was ∼250 nm (Fig. S1).

Following the −CN displacement step, the poly-[Fe(vbpy)]$_3^{3+/2+}$ couple shifts cathodically by 0.51–0.52 V vs. Ag/Ag$^+$ (28). The change in film structure is also shown in UV-vis spectra (Fig. S2). There is a red shift in the visible absorption bands for the d$\pi$(Fe$^{II}$) → π* (bpy) metal-to-ligand charge-transfer transitions following −CN replacement. The metal ions were added by immersing poly [Fe(vbpy)$_3$][CN]$_2$/GCE in solutions containing different ratios of Cu(II) and Ag(I). Addition of the metal ions was evident by shifts in UV-vis spectra with a blue shift observed upon addition of the ions. After binding to the metal ions, the cyanato group becomes a better π-acceptor, stabilizing the d$\pi$ levels, decreasing the d$\pi$ → π* energy gap (28). Following addition of the ions, a single-pulse electrodeposition at −1.7 V vs. Ag$^+$ for 30 s was carried out which led to rapid reduction of the cyano-bound Cu(II)/Ag(I) ions to Cu(0)/Ag(0).

Fig. 1C characterizes the surface morphology of the polymerized electrode. The polymer film has an open porous structure which presumably enhances mass transport during electrochemical reactions (30). The nanoparticulate structure is not obvious in the cross-sectional image in Fig. S1 because the particle sizes were too small to resolve by SEM. The average (Cu)$_2$(Ag)$_3$ particle diameter was 6 ± 2 nm as characterized by the transmission electron microscope (TEM) images in Fig. 1D. This small particle size is documented in uniform distributions of particles prepared by direct electrodeposition (Table 1). The X-ray photoelectron spectroscopy (XPS) spectrum in Fig. 1E shows the characteristic metallic Ag 3d$_{5/2}$ band at 366.8 eV and a mix of metallic Cu and its oxide form by XPS in Fig. 1F (31, 32). The appearance of oxide

![Scheme 1](image-url)
in the Cu sample is not surprising because the Cu nanoparticles are easily oxidized, especially when small (31, 33). Based on the binding energies for Cu and Ag from XPS measurements, compared with their monometallic forms (Fig. S3), in the Cu–Ag particle mixtures, there are separate Cu and Ag nanoparticle clusters rather than mixed-metal alloys. This in contrast to earlier results described for clusters of Cu,Pd, where electrochemical formation of clusters of the alloy was observed (2). The difference in behavior may be due to differences in the electrochemical deposition methods. Single-pulse electrodeposition provides a large

![Graphical images](image)

**Fig. 1.** (A) Room-temperature CVs showing the electropolymerization of 1 mM [Fe(vbpy)$_3$]$_3$[PF$_6$]$_2$ on a GCE in 0.1 M TBAPF$_6$/MeCN at 250 mV s$^{-1}$. (B) CV of the poly-[Fe(vbpy)$_3$]$_{2+}$ couple before replacement of -vbpy (black solid line) and after replacement (gray solid line) at 100 mV s$^{-1}$ in 0.1 M TBAPF$_6$/MeCN, room temperature. (C) SEM image for a (Cu)$_m$(Ag)$_n$/80-layer-poly[Fe(vbpy)$_3$][PF$_6$]$_2$/GCE surface. (D) TEM image and size distribution (Inset) for (Cu)$_2$(Ag)$_3$ nanoparticles; and XPS spectra for Ag (E) and Cu (F) in (Cu)$_2$(Ag)$_3$-polymer-GCE.
driving force over a short period of time, initially with selective deposition of the more reducible metal. The surface atomic ratio of Cu and Ag was determined by XPS with at least three parallel measurements for each sample.

During the electrodeposition process, nucleation and growth from within the particle occur sufficiently rapidly to separate the two effects completely (34). Under normal conditions, with high concentrations of metal ions in the external solution at high applied potentials, large particle sizes with a broad size distribution would be expected (34). In the strategy adopted here, CN\(^-\) coordination plays a critical role in dictating particle size and distribution. Electrodeposition, under the same condition but without the CN\(^-\) ligand, resulted in the appearance of a film for Cu and a large flake for Ag as shown in Fig. S4.

Presumably, the diluted concentration of metal ions in the electrodes, by coordination to the CN\(^-\) ligand, decreases local interactions resulting in a decrease in particle size (34).

The electrocatalytic reactivities of the nanoparticles of the polymer-stabilized, (Cu\(_{m}\)Ag\(_n\))/GCE electrodes for CO\(_2\) reduction were evaluated in 0.5 M KHCO\(_3\) with 8 ppm of benzotriazole (BTA, Scheme 2) added. To increase the solubility of CO\(_2\), all experiments were performed at 0 °C (35). The products of CO\(_2\) reduction were identified and quantified by \(^1\)H NMR in the liquid phase, and by GC for the headspace gaseous products. This (Cu\(_{m}\)Ag\(_n\))/polymer/GCE assembly showed a stable catalytic current over extended electrolysis periods as shown in Fig. S5.

The 8e\(^-\) product (Table S1), CH\(_3\)COO\(^-\) (Fig. 2A), is a highly reduced product. Its appearance is unusual because of the difficulties in overcoming high-energy barriers for C–C formation on surfaces at low temperatures. Its appearance as the major liquid product at low temperatures is one of the few examples in CO\(_2\) reduction chemistry (21). Other products that appear include formate in the liquid phase and CO and methane in the gas phase. A control experiment was conducted using the identical parameters except N\(_2\) was used in place of CO\(_2\). Under this condition, no product peaks were observed in the 1H NMR (Fig. S6). The major product in the background is hydrogen from reduction of the solvent.

The appearance of acetate by the Cu\(_{m}\)Ag\(_n\) clusters led to a more detailed investigation. The results of a study in which the surface metal atom composition was varied are shown in Fig. 2B. Data in the figure appear for acetate generation from the clusters Cu, Cu\(_3\)Ag, Cu\(_2\)Ag, Cu\(_2\)Ag\(_3\), and Ag in CO\(_2\) saturated 0.5 M KHCO\(_3\) at 0 °C at E = −1.53 vs. RHE over periods of 1 h. Based on the data in the figure, there was an increase in the appearance of acetate as Ag was added to the nanoparticles with a maximum reached at 5.5% for Cu\(_2\)Ag\(_3\) clearly showing that surface metal composition plays an important role in acetate formation.

The influence of BTA on CO\(_2\) reduction was also investigated with the reactive Cu\(_2\)Ag\(_3\) cluster mixture. As shown in Fig. 2C, CO\(_2\) reduction by the Cu\(_2\)Ag\(_3\)/polymer/GCE electrode, at 0 C at −1.53 V vs. RHE for 1 h, gave acetate and methane at 5.5% and 1.8% with 8 ppm added BTA. Without BTA the values were 0% acetate and 0.3% methane. Similar results were
The potential dependence of acetate generation by the \((\text{Cu})_2(\text{Ag})_3\) cluster was also investigated. Faradaic efficiencies were measured for \((\text{Cu})_2(\text{Ag})_3\) cluster on the surface, further reduction of acetaldehyde would give acetate as the final product (40).

The mechanism of \(\text{C}–\text{C}\) formation is still debatable. From the data in Fig. 2B, addition of Ag clusters to the surface plays an important role with acetate maximized as a product for the cluster pair \(\text{Cu}_2\text{–Ag}_3\). Ag is a known catalyst for \(\text{CO}_2\) reduction to CO with insight on mechanism from calculations by Peterson and Nørskov (37). Once formed by loss of \(\text{CO}_2\) from the surface, \(\text{CO}\) (gas) is favored thermodynamically as shown in Scheme 3. Cu, on the other hand, has a moderate ability to adsorb and desorb \(\text{CO}\) (37). A possible contributor to acetate production may be Ag-catalyzed formation of CO followed by its capture on neighboring Cu sites for \(\text{C}–\text{C}\) bond formation, Scheme 3. A similar observation was made by Yeo and coworkers (3) for phase-segregated CuZn nanoparticles. In the mechanism in the scheme, acetate could be produced after a series of hydroxylation and electron transfer steps (21).

In an alternate route, CO insertion (3, 38, 39) as observed by Kenis and coworkers (38) on pure Cu surfaces could also occur in ethanol generation. Following \(\text{CO}_2\) reduction to \(-\text{CH}_2\) on the surface of Cu, dimerization of the latter with free CO from Ag would occur to give the \(\text{C}–\text{C}\) bond on the surface. Once formed on the surface, further reduction of acetaldehyde would give acetate as the final product (40).

Conclusion

We have introduced here the details of a well-defined electrochemical procedure for preparing a family of \((\text{Cu})_m(\text{Ag})_n\) clusters on an underlayer of polyp(Fe(vbpy))3][PF6]2\(\text{GCE}\). Monodispersed, ultrasmall, \(-n\text{–}n\) nm particles were obtained by electroposition within the films to give nanoparticles that are among the smallest particle sizes available by this technique. In their reduction chemistry, a key factor is reduction of \(\text{CO}_2\) with an enhancement by added BTA. The ability of clusters to undergo \(\text{CO}_2\) reduction to acetate is highly dependent on the mole fraction ratio in the \((\text{Cu})_m(\text{Ag})_n/\text{polymer/GCE\ mixtures.\ In the sequence of clusters, the most efficient results for acetate were obtained for \((\text{Cu})_2(\text{Ag})_3/\text{polymer/GCE\ films with a faradaic efficiency of 21.2% for acetate at }-1.3 \text{ V vs. RHE in 0.5 M KHCO}_3\ with 8 ppm of BTA at 0 °C.}

Methods

Electrochemical Measurements. All of the electrochemical measurements were performed on a CH1601 D potentiostat station (CH Instruments, Inc.) with a three-electrode setup by using a Pt mesh as the counterelectrode, a Ag (for nonaqueous system) and a saturated calomel electrode (for aqueous system) as the reference electrode, and a GCE as the working electrode. The GCE was first polished with a decreasing size of 1.0- and 0.95-μm alumina lapping compounds for 5 min each and followed by sonication in an ultrasonic bath before use. The potential used for \(\text{CO}_2\) reduction reaction (CO2RR) is corrected to RHE to make comparison with literature.

Electrode Fabrication. The polymerization process was carried out in a nitrogen-saturated solution containing 1 mM polyp(Fe(vbpy))3][PF6]2 in 0.1 M TBAPF6\(\text{CH}_3\text{CN. The GCE was then immersed into this well degassed solution to perform consecutive scans to get polyp(Fe(vbpy))3][PF6]2\text{GCE.\ This electrode was then transferred into 0.1 M TBAPF6\(\text{CH}_3\text{CN\ solution and left for 20 min to allow full replacement of }-\text{CN\ with }-\text{bpy. Before being put into solution with Cu/Ag, the formed dicyano film/GCE was washed with MeCN and dried. After 20 min of incorporation in the metal ion precursor solution, the electrode was cleaned with MeCN and transferred into a nitrogen saturated 0.1 M TBAPF6/MeCN to run electrodeposition under }-1.7 \text{ V vs. Ag for 30 s. Aggregation of particles were observed with longer electrodeposition time.}

Detailed product analysis and CVs are presented in Supporting Information.

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