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Size-dependent reactivity of gold-copper bimetallic nanoparticles during CO_2 electroreduction

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ABSTRACT

New catalysts are needed to achieve lower overpotentials and higher faradaic efficiency for desirable products during the electroreduction of CO_2. In this study, we explore the size-dependence of monodisperse gold-copper alloy nanoparticles (NPs) synthesized by inverse micelle encapsulation as catalysts for CO_2 electroreduction. X-ray spectroscopy revealed that gold-copper alloys were formed and were heavily oxidized in their initial as prepared state. Current density was found to increase significantly for smaller NPs due to the increasing population of strongly binding low coordinated sites on NPs below 5 nm. Product analysis showed formation of H_2, CO, and CH_4, with faradaic selectivity showing a minor dependence on size. The selectivity trends observed are assigned to reaction-induced segregation of gold atoms to the particle surface and altered electronic or geometric properties due to alloying.

1. Introduction

Alloying is a powerful technique to improve the reactivity of metal nanocatalysts by influencing their morphological, chemical, and electronic properties [1–3]. For example, adding a second metal can induce strain or changes in the electronic structure of a catalyst, altering the interaction of reactive species with its surface [4]. Alternately, a secondary metal may provide an alternative active site which facilitates a different reaction step or works as an isolated active site [5]. One reaction where alloyed catalysts may provide remarkable improvement in catalyst activity and selectivity is the electroreduction of CO_2. Currently, Cu shows the most promise as a catalyst for this reaction since it can produce hydrocarbons, but only at high overpotentials [6–9]. Au is also a promising material since it can selectively generate CO at moderate overpotentials [10,11]. Despite these results, low-cost catalysts with high selectivity and efficiency for CO_2 reduction to valuable products are yet to be discovered.

Using density functional theory (DFT), Hansen et al. have shown that the unique hydrocarbon selectivity of Cu can be linked to its optimal binding to the CO* and COOH* intermediates in comparison to other metals [12]. These results indicate that the reactivity of Cu could be further improved by tuning its binding properties to different intermediates, although the scaling relations between these binding energies must first be broken [13]. Several strategies for achieving this have been proposed, including nanostructuring the Cu surface [14] or adding ligands to an active metal center [15], but the most promising may be introducing a secondary metal to create an alloy catalyst [13,16].

Recently, several experimental and theoretical studies have explored the reactivity of bimetallic catalysts during CO_2 electroreduction [5,17–26]. In particular, several studies have focused on copper-gold bimetallics, due to the reactivity of both of these metals [18,27–36]. Composition dependent studies on bulk Au-Cu alloys and 10 nm Au-Cu nanoparticles (NPs) indicate that hydrocarbon production is favored with increasing Cu content, although not surpassing that of pure Cu, while increasing Au content favors an increase in CO selectivity [29]. In order to understand the reactivity of AuCu bimetallic catalysts, it is crucial to understand the structure and stability of the catalysts during the reaction. Monzó et al. investigated Au core Cu shell NPs for CO_2 electroreduction, arguing that trends in reactivity may be explained by strain effects in the Cu shells of different thickness [31]. However, it is important to consider that Cu monolayers on an Au surface can be highly unstable under electrochemical conditions, and Au may segregate to the surface and alloy with Cu [30,37]. In addition, previous stud-

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ies on AuCu CO_2 electroreduction catalysts have been restricted to bulk-like surfaces [27,35] or NPs 10 nm or larger in size [29,31–33], although NPs smaller than 10 nm are known to have widely different reactivity than their bulk counterparts [38,39]. It is also important to consider the oxidation state of the metals in the NP surface and its evolution during the reaction, since oxide derived Cu nanostructures have shown widely improved reactivity during CO_2 electroreduction [40], and a secondary metal may alter the stability of such oxides.

In this study, we address the structure-dependent reactivity of AuCu bimetallic NPs for CO_2 electroreduction using well-defined model NP catalysts less than 10 nm in size. NPs in the size range from 1.4 to 24 nm were synthesized using inverse micelle encapsulation and characterized using microscopy and X-ray spectroscopy. Although a significant increase in activity was found for smaller NPs, the selectivity was found to have only slight size dependence, in stark contrast to monometallic Au and Cu NPs.

2. Experimental

2.1. Nanoparticle synthesis

Monodisperse AuCu bimetallic NPs were synthesized using the inverse micelle encapsulation technique. Poly(styrene-*b*-2-vinyl pyridine) diblock copolymers (Polymer Source, Inc.) with different molecular weights (Table 1) were dissolved in toluene to form reverse micelles. $HAuCl_4$ and $CuCl_2$ were added to the solutions and stirred for two days. The resulting metal loaded micelle solutions were dip-coated onto the support (silicon wafers or glassy carbon), and then the encapsulating polymers were removed using 20 min of oxygen plasma at 20 W. The absence of the C 1 s signal in X-ray photoelectron spectra (XPS) measured on silicon wafer-supported samples was used to ensure the plasma etching conditions were sufficient to completely remove the polymers. For the synthesis of the electrodes, the dip-coating and plasma etching steps were repeated three times to increase the loading of NPs on the glassy carbon.

2.2. Structural and chemical characterization

Atomic force microscopy (AFM) was used to determine NP size, interparticle distance, and geometrical surface area of our NP catalysts. AFM was acquired using a Digital Instruments Nanoscope-III microscope on ligand-free AuCu NPs dip-coated onto SiO_2/Si(111) wafers. The interparticle distance d was estimated as $d = \frac{1}{\sqrt{\sigma}}$ by measuring the NP density σ and assuming hexagonal arrangement. The metal NP surface area was estimated by using the NP height and NP density from AFM and calculating the NP surface area per area of support, assuming spherical NPs. The latter was used as geometrical metal surface area for the normalization of the electrochemical currents.

XPS was measured with a monochromatic Al Kα source (1486.6 eV) in an ultra-high vacuum (UHV) system with 2×10^{-10} mbar base pressure (Phobios 150, SPECS GmbH). Data were aligned to the Si^0 2p peak at 99.3 eV. X-ray absorption fine-structure spectroscopy (XAFS) was measured at beamline 10-ID-B of the Advanced Photon Source at Argonne National Laboratory. For XAFS, 7.9 nm AuCu NPs supported on a carbon foil were measured in air in fluorescence geometry at the Cu K and Au L_3 edges. Data were analyzed using the Athena and Artemis software from the IFEFFIT package [41], and fitting was performed using FEFF 8 calculations [42].

2.3. Electrochemical methods

CO_2 electroreduction was performed in a three electrode electrochemical cell. A platinum mesh 100 was used as counter electrode, and a leak-free Ag/AgCl electrode was used as reference electrode. The working electrode was the AuCu NPs supported on glassy carbon plates. The electrolyte was 0.1 M $KHCO_3$, and CO_2 was bubbled at a constant flow rate of 30 mL/min from the bottom of the cell (pH = 6.8). Every measurement was started with a linear voltammetric sweep performed with a scan rate of −5 mV/s between E = +0.05 V_{RHE} and the working potential (−1.2 V_{RHE}), followed by a chronoamperometric step for 10 min. Gas products (H_2, CO, and CH_4) were monitored using a gas chromatograph (Shimadzu GC 2016) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The products were measured at −1.2 V_{RHE} to ensure high enough production rates for reliable GC detection over our low loading samples. The signal from a blank glassy carbon electrode was subtracted from all electrochemical data shown here.

3. Results and discussion

For this study, AuCu NPs ranging from 1.4 to 24 nm in size were synthesized using an inverse micelle encapsulation method. Since the surface of the glassy carbon electrodes is rough, the NPs were deposited onto silicon wafers to accurately characterize their morphology using AFM. Fig. 1 and Fig. S1 in the Supplementary material show AFM images of three coats of AuCu NPs supported on SiO_2/Si(111), with size histograms shown in Fig. S2 in the Supplementary material. Table 1 lists the synthesis parameters used for the five samples, along with the morphological parameters acquired from AFM including the NP size, interparticle distance, and the surface area used for normalization of the electrochemical data. The AFM results show that the NPs could be synthesized with a high degree of size control, and narrow size distribution was achieved for the four smaller NP sizes. The largest 24 nm NPs had a wider size distribution and resulted in a bimodal size distribution, as shown in Fig. S2e in the Supplementary material. Further discussion of this sample is given in the Supporting information.

XPS was used to characterize the composition and chemical state of the NPs in their initial as prepared state. The composition of the NPs was determined by quantifying the Au 4f and Cu $2p_{3/2}$ peaks measured on the as prepared NPs supported on SiO_2/Si(111). Close to 50-50 Au-Cu composition was calculated for each sample, as shown in Table 1. It should be noted that XPS is a surface sensitive technique and may not probe the bulk of the larger NPs.

XPS was also used to investigate the oxidation state and alloying of the Au and Cu in the NPs. Fig. 2 shows the Au 4f and Cu 2p core level regions measured on the 7.9 nm AuCu NPs supported on SiO_2/Si(111). Fig. 2a and b shows data acquired immediately after *ex situ* O_2 plasma treatment and transfer in air to the UHV system for XPS measurement. After O_2 plasma, the Au 4f region shows mainly Au^{3+} peaks, indicating that the NPs contained mostly Au_2O_3 species. Small Au^0 peaks were also measured, and the Au^0 $4f_{7/2}$ peak agrees with bulk metallic gold at 83.9 eV. The Cu 2p region shows only Cu^{2+} species with the characteristic satellite peaks at higher binding energies. Only the Cu $2p_{3/2}$ peaks were fit, since a sloped background exists at high binding energies due to overlap with the O LMM Auger lines. The Cu $2p_{3/2}$ peak can be deconvoluted into two peaks which agree with CuO and $Cu(OH)_2$ species. These results show that the NPs are heavily oxidized in their as prepared state due to the O_2 plasma treatment employed during the synthesis.

In order to confirm that true alloyed NPs were formed, the oxidized NPs were thermally reduced under mild reducing conditions