Highly Active and Durable Cu$_{x}$Au$_{(1-x)}$ Ultrathin-Film Catalysts for Nitrato Electroreduction Synthesized by Surface-Limited Redox Replacement

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ABSTRACT: Cu$_{x}$Au$_{(1-x)}$ bimetallic ultrathin-film catalysts for nitrato electroreduction have been synthesized using electrochemical atomic layer deposition by surface-limited redox replacement of Pb underpotentially deposited layer. Controlled by the ratio of [Cu$^{2+}$] ions and [AuCl$_4^-$] complex in the deposition solution, the alloy film composition (atomic fraction, x in the range of 0.5–1) has been determined by X-ray photoelectron spectroscopy and indirectly estimated by anodic stripping voltammetry. The catalytic activity and durability of Cu$_{x}$Au$_{(1-x)}$ thin films, Cu thin film, and bulk Cu have been studied by one- and multiple-cycle voltammetry. The synthesized Cu$_{x}$Au$_{(1-x)}$ thin films feature up to two times higher nitrate electroreduction activity in acidic solution compared to bulk and thin-film Cu counterparts. Highest activity has been measured with a Cu$_{0.70}$Au$_{0.30}$ catalyst. Durability tests have demonstrated that Cu thin films undergo rapid deactivation losing 65% of its peak activity for 92 cycles, whereas Cu$_{0.70}$Au$_{0.30}$ catalysts lose only 45% of their top performance. The significantly better durability of alloy films can be attributed to effective resistance to poisoning and/or hindered dissolution of Cu active centers. It has been also found that both Cu$_{x}$Au$_{(1-x)}$ and pure Cu thin films show best electroreduction activity at lowest pH.

1. INTRODUCTION

In the last few decades, nitrate pollution has gradually become a severe environmental problem. The undesired contamination with nitrates is largely due to the byproduct of fertilizers and nuclear and animal waste. A high concentration of NO$_3^-$ ions in drinking water poses a health hazard to human beings. It has been proven that these hazards could result in methaemoglobinemia (blue-baby syndrome) or even potentially cancer. The global trend for environmental compatibility has led to increasing demand for removing nitrates using environmental friendly approaches that meet energy conservation standards. There are a couple of methods that have been developed to collect or eliminate NO$_3^-$ ions from aqueous media. Some of these include physicochemical means, biological denitrification, and electrochemical reduction approaches. Among all, reverse osmosis and ion exchange are two major commercial ways to remove nitrate from drinking water. However, the need for post-treatment sludge generation and high membrane costs associated with said approaches significantly restricts the expansion of their application. Because of the controllable selectivity, environmental compatibility, and relatively low cost, the electro-reduction of nitrate through a metallic or bimetallic catalyst has been considered the most promising technique for denitrification. An additional advantage of this approach is that with application of different reduction routes along with their elimination/removal, the NO$_3^-$ ions could be converted into a variety of useful chemicals, such as ammonia and hydroxylamine.

Electroreduction of nitrate in acidic solution has been investigated by many researchers. Dima et al. have reported comprehensively on the nitrate electroreduction activity of coinage metals and transition metals in acidic solution. It is concluded that Cu known to produce ammonia as the main reduction product is the most active catalyst among coinage metals. Studies detailing the mechanism of nitrate electro-reduction on poly- and single-crystalline Cu electrodes have also been found in the literature. Overall, an eight-electron reduction route with a standard reduction potential $E^0 = 0.80$ V versus H$^+/H_2$ (normal hydrogen electrode, NHE) as presented below is believed to be the dominating nitrate electroreduction process on Cu

$$\text{NO}_3^- + 8e^- + 9H^+ \rightarrow 3\text{H}_2\text{O} + \text{NH}_3$$

In more detail, the mechanistic study identifies the above reduction process as a multiple-step process. As a result of different steps of this process, a variety of intermediates such as NO and NO$_2^-$ have been reported. The research on single-crystal faces of Cu with different orientations also suggested slight differences in the reduction mechanism and catalytic
performance. Overall, the main drawbacks reported for using Cu as catalyst for nitrate electroreduction are associated with its oxidative dissolution and surface poisoning/passivation leading to catalyst loss and deactivation, respectively. According to proposed reasons for catalyst deactivation, the spontaneous oxidation of Cu and competitive adsorption of ions other than NO$_3^-$ (mostly H$^+$) are deemed key factors in the performance deterioration of the monometallic Cu. To address these drawbacks, many research groups synthesized bimetallic catalysts to boost the catalyst’s activity and enhance its durability. Vorlop and Tacke first synthesized bimetallic catalysts consisting of both noble metal and promoter metal. The mechanism and performance of bimetallic catalysts like Pt–Cu and Pd–Cu have been studied by many groups. The general mechanism for nitrate electroreduction at a bimetallic catalyst in an acidic environment is summarized in the following reactions

$$\text{H}^+ + e^- \rightarrow_{\text{noble}} \text{Me} \rightarrow \text{H}_{\text{ads}}$$  \hspace{1cm} (2)

$$\text{NO}_3^- \rightarrow_{\text{promoter}} \text{Me} \rightarrow \text{NO}_3^-_{\text{ads}}$$  \hspace{1cm} (3)

$$\text{H}_{\text{ads}} + \text{NO}_3^-_{\text{ads}} \rightarrow \text{NO}_2^-_{\text{ads}} + \text{OH}^-$$  \hspace{1cm} (4)

This mechanism indicates that H$^+$ ions tend to discharge and adsorb preferentially on the noble-metal surface. The adsorbed H atoms then engage more in facilitating the nitrate reduction rather than poisoning the promoter metal. Generally, it is believed that the adsorbed H atoms could transfer to the O moieties of NO$_3^-$ ions at the catalyst surface to form OH$, thus facilitating the entire reduction process. Although impact on catalysts’ activity of anions other than NO$_3^-$ has also been reported, most of the mechanistic studies suggest that optimal catalysts for nitrate electroreduction are bimetallic structures consisting of two different types of active sites: noble metal sites responsible for the NO$_3^-$ adsorption followed by reduction and noble-metal sites providing for H adsorption, promoter stabilization, and product control.

Several synthetic methods for mono- or bimetallic catalysts have been reported in the literature. Some groups employ electrodeposition methods, which lead to burying of a large amount of noble metal under the active surface. Other groups synthesize nanoparticle bimetallic catalysts. Most tests of these catalysts focus on the impact of intermetal interactions on the nitrate electroreduction activity. The results suggest that the activity could be enhanced by improving the mixing homogeneity between noble and promoter metals. However, the nanoparticle preparation method is often time-consuming and complex, which generally limits its application. In this context, electrochemical atomic layer deposition (E-ALD) of ultrathin bimetallic films appears to be the optimal method because of its ability to maximize the utilization of noble metal under strict deposition control in realization continuous films as thin as a few monolayers (MLs). The E-ALD utilizing a surface-limited redox replacement (SLRR) reaction has also been proven to provide the best homogeneity among all electrochemical deposition approaches.

As recently summarized in a review article, our group has developed a one-cell approach for realizing the E-ALD by SLRR protocol and thus making it convenient for synthesis of low-Pt-loading catalysts. Using that approach and replacing underpotentially deposited (UPD) Pb, Cu, and H layers, we successfully synthesized Pd, Pt, and Pt–Cu ultrathin films on flat and nanoporous gold surfaces. The main objective of this work is to investigate the functionality of gold as noble-metal constituent in bimetallic catalysts for nitrate electroreduction. The emphasis is on the evaluation of gold’s ability to (i) stabilize copper, (ii) minimize copper poisoning, and (iii) facilitate the nitrate reduction reaction. In this work, Cu$_{1−x}$Au$_x$ thin-films were synthesized via the SLRR-based method, and chronopotentiometry was used to monitor the growth process. After the deposition, Pb UPD cyclic voltammetry (CV) was used to assess the surface roughness of as-grown catalysts. Anodic stripping voltammetry (ASV) and X-ray photoelectron spectroscopy (XPS) were employed to confirm the atomic ratio (elemental content) of the prepared catalyst. The activity and durability of Cu–Au catalysts are tested by cyclic voltammetry (CV) and chronoamperometry. The catalytic behavior of Cu–Au films with different compositions is also discussed in this paper. To contemplate the influence of free H$^+$ ion concentration, the pH was varied from 1.62 to 5.50 in the testing of Cu–Au bimetallic and plain Cu catalysts. The behavior of bulk copper and Cu–Au in different pH solutions was also studied.

2. RESULTS AND DISCUSSION

2.1. Cu–Au and Cu Ultrathin-Film Synthesis through SLRR on Au Substrate. Polycrystalline Au electrodes were used as a substrate for Cu$_{1−x}$Au$_x$ and Cu ultrathin-film deposition. Pb UPD CV known to produce signature type curves for different crystallographic orientations of Au was employed to characterize the surface of the Au substrate before each experiment as both the ultrathin-film growth and nitrate reduction have shown dependence on the substrate crystallographic orientation. Figure 1 shows a representative Pb UPD
curve on Au (poly) electrodes used as a substrate in this study. Reference to such curves for comparison could be found in other papers of our group as well. The distinct presence of a sharp and narrow split cathodic peak at 0.2 V versus Pb/Pb\(^{2+}\) suggests a dominating (111) orientation of the Au polycrystalline electrodes. There are some additional contributions of (100) and (110) shown by other peaks. The overall shape of the CV curve in terms of width and height of the peaks ascertains the suitability of the Au electrodes as substrates for Cu–Au and Cu deposition.

The growth of Cu and Cu–Au bimetallic ultrathin films was conducted by an SLRR approach employing Pb UPD as a sacrificial layer and realized in one-cell configuration. Thereby, for the Cu film, Cu\(^{2+}\) ions replace spontaneously the predeposited Pb UPD layer, whereas for the Cu–Au ultrathin film, the replacement will be powered by both Cu\(^{2+}\) ions and [AuCl\(_4\)]\(^{-}\) complex. To avoid further displacement of Cu by [AuCl\(_4\)]\(^{-}\) in the course of alloy film deposition, it is essential to strictly control the cut-off potential (C-OP). Figure 2 shows a representative potential transient for a set of 15 “building block” SLRR cycles performed on Au (poly) electrodes to deposit a Cu–Au ultrathin film. The growth procedure is initiated from the open-circuit potential (OCP) of the substrate, followed by the application of a negative pulse to a potential of −0.850 V (−0.05 V vs Pb/Pb\(^{2+}\)) for 1 s. Because of the substantial concentration difference of Cu\(^{2+}\), AuCl\(_4\)\(^{-}\) complex, and Pb\(^{2+}\) ions, only negligible amounts of Cu and Au are deposited in that 1 s of Pb\(_{\text{UPD}}\) layer formation. Then, after the release of the potential control, the Cu\(^{2+}\) ions and AuCl\(_4\)\(^{-}\) replace the Pb atoms causing a potential excursion back to OCP. The film thickness could be controlled by the number of administered SLRR events. In Figure 2, the OCP transients depict a replacement rate that slows down from the first to the third SLRR cycle because of the substrate change (from Au to Cu) and then gradually levels off with an increase of the Cu–Au film thickness, suggesting a dominant activation control for the exchange reaction.

When it comes to the SLRR co-deposition of Cu–Au bimetallic ultrathin film, it is very important to determine the cut-off potential (C-OP) where the next Pb\(_{\text{UPD}}\) layer formation needs to be applied after the completion of the previous SLRR cycle. The C-OP in the case of Au–Cu deposition must be negative to the OCP so that any potential displacement of already deposited Cu atoms by AuCl\(_4\)\(^{-}\) species be strictly eliminated. A similar strategy was employed in another work of our group whereby Pt\(_x\)Cu\(_{1−x}\) alloy thin films were deposited by SLRR in one-cell setup. The same potential approach is applied here as well to realize CuAu ultrathin film layers (Figure 3). Figure 3 shows the replacement process at the [Cu\(^{2+}\)/[AuCl\(_4\)\(^{-}\)] solution ratio 1:1. The low-sloped part of the curve between −0.4 and −0.2 V where likely most of the redox replacement process takes place, one can clearly see regions with two different slopes. The first range of the curve featuring steeper slope is most likely associated with the replacement of Pb by both Cu\(^{2+}\) and AuCl\(_4\)\(^{-}\). The following second range features slower potential change, likely associated with a process with impeded kinetics. Most likely, that process could be the one mentioned, where the replacement of already deposited Cu atoms by [AuCl\(_4\)\(^{-}\)] complex species occurs. Should the later process be enabled the resultant deposit will be substantially richer in Au in comparison with the targeted Au/Cu atomic fraction ratio in the deposited alloy. Hence, the C-OP must be chosen negatively to the potential indicated by the arrow in Figure 3.

2.2. Anodic Stripping of SLRR-Deposited Cu\(_{x}\)Au\(_{1−x}\) Ultrathin Film. The overall amount of deposited metals in the

![Figure 2. Potential transient depicting the growth of Cu–Au on Au (poly) using 15 SLRR cycles of Pb UPD. The solution composition is 0.5 mM Cu(ClO\(_4\))\(_2\), 0.5 mM NaAuCl\(_4\), 1 mM Pb(ClO\(_4\))\(_2\), 10 mM HClO\(_4\), and 100 mM NaClO\(_4\).](Image 17678)

![Figure 3. Complete OC potential transient of the replacement process after 1 s potential pulse for Cu–Au ultrathin-film growth. The solution composition is 0.5 mM Cu(ClO\(_4\))\(_2\), 0.5 mM NaAuCl\(_4\), 1 mM Pb(ClO\(_4\))\(_2\), 10 mM HClO\(_4\), and 100 mM NaClO\(_4\).](Image 17686)
prepared plain Cu and Cu–Au bimetallic thin films could be obtained by ASV. Although the stripping involves only Cu, the analysis of the stripping experiment taking into account also the overall deposition charge allows for quantitative analysis of the amount of deposited Cu and Au from different solutions with molar ratio of [Cu^{2+}]/[AuCl_4^{-}] = 1:1, 2:1, and 4:1. Figure 4 shows a plot of stripping curves obtained by ASV for electrodedeposited Cu. Similarly with Cu earlier work of our group where Cu and Au were co-dealloy at different potential ranges as seen in the second peak in the range 0.60–0.75 V. The alloys with more Au, such as Cu/Au = 2:1, contain more CuAu and CuAu_3 phases, which will show up in the third peak (0.80–1.00 V).

Further analysis of the ASV curves (Figure 4) can enable an estimate of the overall Cu content in the SLRR co-deposited Au–Cu alloys, which in turn can be used to further understand the relationship between [Cu^{2+}]/[AuCl_4^{-}] solution ratio and the composition of the accordingly deposited alloy. Table 1 summarizes the total dealloying charge as well as the dealloying charges in different potential ranges determined by ASV for Cu–Au ultrathin film with different compositions. All reported charges have been corrected with the background charge measured under identical conditions on pure Au electrode. A closer look at the data in Table 1 suggests that with the increase of Cu atomic fraction in the deposited alloy, more of the nonbonded or low coordination alloyed Cu atoms will take part in the dissolution process, resulting in most of the Cu being dissolved at most negative potential range. Compared with our previous results on the dealloying of Cu–Au thin films synthesized by bulk co-deposition, the use of SLRR co-deposition in this work suggests the presence of more alloyed Cu, which on dealloying (Figure 4 and Table 1) results in more charge in the second and third anodic potential ranges. This phenomenon is possibly due to enhanced homogeneity in the Cu–Au alloy layer deposited by SLRR through layer-by-layer deposition. A more detailed consideration and further analysis of data presented in Table 1 along with accounting for the number of administered SLRR cycles and the charge density of one ML of Pb, which is same on both Cu and Au polycrystalline electrodes, could be used to estimate quantitatively the atomic fraction of Cu/Au ratio in the SLRR-deposited alloys. More specifically, such an estimate could be done knowing that 15 SLRR cycles will produce a one-at-a-time basis, a total of 15 MLs of Pb_{Pb-Pb} with a total charge of 4500 μC cm^{-2} (300 μC cm^{-2} for 1 ML Pb on Au_{poly}). Then, Pb will further be replaced at OCP by Cu^{2+} and AuCl_4^{-} at an assumed efficiency of 94% as suggested by earlier experience with the growth of pure Cu by SLRR. This means that the total deposition charge for the growth of our alloy films in the 15-cycle run will be 4230 μC cm^{-2}. For [Cu^{2+}]/[AuCl_4^{-}] = 1:1, one measures a total Cu stripping charge of 1994 μC cm^{-2} (see Table 1) that is then corrected with the background charge (620 μC cm^{-2}). As a result of this correction presented in the first row of the respective cell in Table 1, one obtains a net Cu stripping charge of 1374 μC cm^{-2} (see the second row of the cell). Finally, assuming that the difference between the corrected total deposition charge.

Table 1. Anodic Stripping Charge Comparison of Cu_{Au(1-x)} Alloys with Different Compositions

| Cu/Au solution ratio and # of SLRR cycles | total stripping charge (μC cm^{-2}) | stripping charge: 1st stage (μC cm^{-2}) | stripping charge: 2nd stage (μC cm^{-2}) | stripping charge: 3rd stage (μC cm^{-2}) | estimated Cu/Au alloy ratio by ASV results |
|-----------------------------------------|------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|
| 1:1 and 15 cycles                       | 1374 (1994–620)                    | 319 (438–19)                             | 419 (505–86)                             | 536 (1051–515)                           | 1:1                                     |
| 2:1 and 15 cycles                       | 1765 (2385–620)                    | 427 (446–19)                             | 582 (668–86)                             | 596 (1111–515)                           | 1:1                                     |
| 4:1 and 20 cycles                       | 3600 (4220–620)                    | 1401 (1420–19)                           | 1367 (1453–86)                           | 830 (1345–515)                           | 2:7:1                                   |

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and Cu stripping charge (1374 μC cm⁻²) is associated with Au fraction in the alloy and taking into account the difference in the oxidation state between Cu and Au in the solution (2:3, respectively), one calculates the atomic fraction ratio Cu/Au in the analyzed alloy to be 1:1.4. More results summarizing the corrected total stripping charge and partial charges in different potential ranges for Cu–Au alloys deposited from solutions with 2:1 and 4:1 Cu²⁺/[AuCl₄]⁻ ratio can be also found in Table 1. On the basis of the respective data and the above described algorithm, the table presents calculated Cu/Au atomic fraction ratios in the respective alloys as well.

### 2.3. Atomic Composition Assessment by XPS

The atomic composition of synthesized Cu–Au ultrathin film could be determined by XPS. The XPS characterization results for Cu–Au alloys deposited in solutions with different ratios of [Cu²⁺] and [AuCl₄]⁻ by 40 SLRR cycles are presented in Figure 5. Specifically, for concentration ratios of [Cu²⁺]/[AuCl₄]⁻ equal to 3:1, 1:1, and 1:2, the analysis of the XPS results yielded Cu/Au atomic composition ratios of 70:30 (2.3:1), 45:55 (1:1.2), and 30:70 (1:2.3), respectively. The Cu and Au contents in the alloy were determined with an error of inhomogeneous distribution of metals on the surface and inaccurate relative sensitivity factors due to the oxidization of metals on the surface, respectively. Compared with the electrochemical dealloying results, the charges were determined with an error of about 5% and the XPS results are more accurate with a percentage error of up to 1.00%. As seen in Table 2, the obtained results by both methods are reasonably close (compare directly alloys deposited in solution with 1:1 [Cu²⁺]/[AuCl₄]⁻ ratio), and both suggest the presence of a higher atomic fraction of Au in comparison with the one that follows directly from the Cu/Au solution ratio. This finding persists as a trend in all other alloy compositions subjected to both characterization approaches even though direct comparison cannot be made because of differences in the Cu/Au solution ratios. Therefore, it can be concluded that Cu atomic fraction in the alloy is always lower than the one following from the specific solution composition. The observed common trend in measured and estimated atomic fractions could be explained by the strong likelihood of secondary galvanic displacement of already deposited Cu atoms by the substantially more noble Au ones. Such secondary displacement is readily enabled by the presence of AuCl₄⁻ complex at potentials that are only slightly positive so that the cut-off potential is chosen inevitably with considerable ambiguity. Overall, regardless of the encountered discrepancy between the solution and atomic fraction ratios of Cu/Au, the analyses of ASV and XPS results indicate that the atomic composition is generally controllable by tuning the [Cu²⁺]/[AuCl₄]⁻ ratio in the growth solution.

### 2.4. Nitrate Electroreduction Activity Tests

In this work, bulk Cu, bulk Au, Cu ultrathin film, and Cu₀.₅₃Au₀.₄₇ ultrathin alloy film deposited in a solution with Cu/Au ratio of 2:1, both produced by 15 SLRR cycles, have been chosen for assessment of catalytic activity in nitrate electroreduction test in 10 mM HClO₄ solutions with and without 10 mM HNO₃. Figure 6 shows the nitrate electroreduction activity of selected catalysts. The violet and the green curves indicate that ultrathin-film Cu shows similar reduction activity as the bulk copper catalyst. Thus, the cathodic current exhibits the first peak at −0.75 V versus mercury–mercurous sulfate electrode (MSE) ascribed elsewhere to the reduction of NO₃⁻ to NO₂⁻ for bulk copper and copper ultrathin film. Going negatively on the CV curve, one sees another peak at −1.00
V versus MSE. That peak is generally attributed to a further reduction of NO$_3^-$ to ammonia or other products.\(^\text{15}\) The onset of the hydrogen evolution reaction (HER) occurs at \(-1.40\) V. The red dotted (alloy) and green dotted (pure Cu) curve both obtained without NO$_3^-$ ions in the solution are provided for comparison with catalysts basically exhibiting only HER activity. The orange curve shows no activity for pure Au and Au catalysts (both deposited by 15 SLRR cycles). The sweep rate is 20 mV s\(^{-1}\).

The reduction behavior of Cu$_{0.53}$Au$_{0.47}$ ultrathin film in the presence of NO$_3^-$ ions appears to be a one-step reduction process. More specifically, unlike pure Cu and Cu ultrathin films\(^\text{17,19,38}\) the reduction curve of Cu–Au bimetallic catalyst features only one peak at \(-1.05\) V versus MSE. This peak is also about 50% higher in the same potential range than the pure Cu one. Negative to that range, the HER starts taking place on the alloy surface at the same potential as pure Cu.

So far, many researchers have proved that polycrystalline Au catalysts exhibit no activity in nitrate reduction scenarios.\(^\text{5,56,57}\) However, the density functional theory (DFT) calculation has proved that H adsorption albeit much weaker than Pt and Pd\(^\text{59}\) still takes place on Au. The Au atoms could be then considered as optimal sites for H adsorption and further reaction instead of centers only holding strongly H atoms on the surface like Pt or Pd. At the same time, Cu is among the best catalysts for nitrate electroreduction,\(^\text{25,58}\) although it has the disadvantages of undergoing spontaneous dissolution in acidic solution\(^\text{20}\) and being prone to passivation with the reduction testing cycles.\(^\text{17,19}\) Therefore, owing to the dramatically different affinities of Au and Cu to nitrate reduction conversions, the Cu–Au bimetallic catalyst appears to support a different reduction mechanism from the pure Cu. This alloy combination exhibits better activity than pure Cu and Cu ultrathin films in the potential range between \(-0.90\) and \(-1.20\) V (second peak position). Possible reasons for this enhanced activity are as follows: (i) In the bimetallic catalysts, Cu atoms could be perceived as sites for nitrate adsorption (see eq 6), whereas Au atoms could be sites for H$^+$ adsorption, as shown in eq 5 in the same potential range. This is in agreement with the results in Figure 6 whereby the pure Au polarization curve (solid orange curve) suggests an ongoing HER activity in the potential range of interest. In turn, this HER activity can provide sufficient amount of adsorbed H as a powerful reducing agent for nitrate reduction, reactivation of passivated Cu sites, and thus for promotion of the entire reaction, as demonstrated by eqs 1 and 7. The equations are listed below

\[
\text{H}^+ + \varepsilon^- \rightarrow \text{Au} - \text{H}_{ads}
\]

\[
\text{NO}_3^- \rightarrow \text{Cu} - \text{NO}_3^-_{ads}
\]

\[
6\text{Au} - \text{H}_{ads} + \text{Cu} - \text{NO}_3^-_{ads} + 2\varepsilon^- \rightarrow \text{NH}_3 + 3\text{OH}^-
\]

(ii) The lattice structure and electronic structure of a Cu–Au bimetallic catalyst is different from pure Cu as directly manifested by a larger lattice parameter and a shift of d-band center.\(^\text{60,61}\) Given that, the binding energy between NO$_3^-$ ions and the Cu–Au catalyst surface may become optimal and thus beneficial for promotion of the reduction reaction. On the other hand, according to the previous calculation, the nitrate establishes bidentate adsorption configuration on both Au and Cu\(^\text{16,62}\) in which two oxygen atoms connect to surface and the other oxygen atom is exposed to solution; hydronium adsorbed on sites surrounded by NO$_3^-$ ions could form a bond with oxygen of neighboring NO$_3^-$ to facilitate the nitrate reduction.

As there is no comprehensive study on the application of Cu–Au catalyst system in nitrate electroreduction process, a further reduction product analysis and DFT calculation will be required in the future for better understanding of this matter.

### 2.5. Effect of Cu/Au Atomic Ratio on Nitrate Electroreduction Activity

In the synthetic part of this work, routines for the SLRR deposition of bimetallic catalysts Cu/Au with atomic fraction ratio from 0.50 to 0.90 have been developed. Figure 7 summarizes results on the influence of the increasing Cu amount on the Cu–Au alloy catalyst activity. It

| Cu/Au solution ratio and # of SLRR cycles | Cu$_{0.45}$Au$_{0.55}$ (by ASV), $x$ is atomic fraction | Cu$_{0.42}$Au$_{0.58}$ (by XPS), $x$ is atomic fraction | atomic fraction ratio in Cu$_{Au(1-x)}$
|---|---|---|---|
| 1:2 and 40 cycles | N/A | Cu$_{0.42}$Au$_{0.58}$ | 1:2.3 |
| 1:1 and 15 cycles (ASV) | Cu$_{0.53}$Au$_{0.47}$ | Cu$_{0.42}$Au$_{0.55}$ | 1:1.4 (ASV) |
| 1:1 and 40 cycles (XPS) | Cu$_{0.53}$Au$_{0.47}$ | Cu$_{0.42}$Au$_{0.55}$ | 1:1.2 (XPS) |
| 2:1 and 15 cycles | N/A | N/A | 1:1 |
| 3:1 and 40 cycles | Cu$_{0.53}$Au$_{0.47}$ | Cu$_{0.42}$Au$_{0.58}$ | 2.3:1 |
| 4:1 and 20 cycles | Cu$_{0.53}$Au$_{0.47}$ | N/A | 2.7:1 |

Figure 7. Correlation between [Cu$^{2+}$]/[AuCl$_4$]$^{-}$ Solution Ratio and Cu Atomic Fraction, $x$ in Cu$_n$Au$_{(1-x)}$ Alloys As Assessed by ASV and/or XPS.
is clearly seen in that all compositions containing between 0.50 and 0.80 fractions of Cu exhibit similar catalytic activity manifesting itself through a curve with one very dominant peak, as already presented in Figure 6 for a Cu0.53Au0.47 catalyst. On a relative basis, maximum activity is obtained with Cu0.70Au0.30 alloy. Higher or lower Cu content leads to relatively lower activity thus making the Cu fraction/activity dependence to look like a volcano shape relationship. With the increase of the Cu fraction in Cu−Au catalysts, the activity decreases to a value same as seen with pure Cu catalyst. It is noteworthy that the transition to two-peak curves occurs when the atomic fraction of Cu is equal or higher than 0.90. For the Cu with an atomic fraction less than 0.50, the nitrate electroreduction activity drastically decreases to that of a pure Au, which is catalytically inactive.

The possible mechanism for this behavior is associated with a change of the atomic fraction ratio on the catalyst surface. When Cu is more abundant on the surface (more than 0.90 atom fraction), the Au sites are undoubtedly less accessible. In that case, the nitrate electroreduction activity curve should be practically identical with the activity of pure Cu. In contrast, if the Cu atomic fraction is less than 0.50 in Cu−Au, the Cu sites for nitrate adsorption will be limited on the catalyst surface, as the dominating phase or element on the catalyst surface could be Au, Cu or Au, respectively; these two catalysts mostly favor the HER that is readily enabled in this potential region. In other words, due to lack of adsorbed NO3− ions, adsorbed H atoms mostly combine with each other to generate H2 gas. As a result, in that case, catalysts become practically inactive in nitrate electroreduction process.

2.6. Catalyst Durability Tests. In this section, nitrate reduction durabilities of pure Cu and Cu−Au have been tested in 10 mM HClO4 + 10 mM HNO3 solution for 100 cycles. Figure 8 shows the CV diagram obtained from pure Cu immersed in the testing solution, whereby the reduction activity decreases substantially with the number of cycles. Figure 9 shows the CV diagram obtained from Cu−Au bimetallic catalysts in the same solution. It is clearly seen that unlike in the previous case, the catalyst retains a high reduction activity with the number of cycles. A quantitative look into the comparison of results presented in Figures 8 and 9 suggests activity decrease for the Cu−Au catalyst to 55% versus a decrease to 35% for the pure Cu catalyst at a potential between −0.9 and −1.1 V after 92 cycles. This comparison clearly proves that Cu−Au catalyst exhibits significantly better durability in the nitrate electroreduction process.

Previous research proves that pure Cu catalysts experience spontaneous dissolution and hydrogen poisoning in acidic solution.5,8,18 Cu0.70Au0.30 bimetallic catalysts show better durability in nitrate electroreduction compared with mono-metallic Cu. One of the explanations for better durability of
Cu$_{0.70}$Au$_{0.30}$ catalyst is due to the usage of noble-metal Au. As largely discussed earlier in this paper, Au stabilizes the Cu by forming a single-phase alloy or intermetallic compounds both being substantially more stable in acidic solution. In addition, some researchers ascribe the passivation of pure Cu catalyst to the adsorbed H atoms that block the Cu sites. It is well known that Au is a weak adsorption substrate for H atoms. Thus, it is deemed likely that the addition of Au could make the Cu active sites less prone to H adsorption as well.

### 2.7. Effect of pH on Nitrate Electroreduction Activity

In this section, the pH dependence of nitrate electroreduction has been studied on pure Cu and Cu$_{0.70}$Au$_{0.30}$ bimetallic catalysts. Figure 10 displays the CV diagram of Cu and respective lack of H$^+$ significantly slows down the nitrate electroreduction reaction. Overall, to increase the nitrate electroreduction activity in the process of nitrates’ removal, it is essential to lower the pH of polluted ground water, which brings another challenge of returning the pH to a neutral value afterward.

#### 3. CONCLUSIONS

Bimetallic Cu–Au ultrathin-film catalysts were first synthesized via the E-ALD method utilizing SLRR of Pb UPD layer. The XPS and anodic stripping results clearly demonstrated that the SLRR method is advantageous for deposition of homogeneous and continuous films with controllable composition and thickness. The nitrate electroreduction activities of Cu–Au ultrathin film, Cu ultrathin film, bulk Cu and bulk Au were also comparatively studied. Our results confirmed that pure Cu catalysts were inactive in the nitrate electroreduction process. In contrast, Cu–Au bimetallic ultrathin films were found to be more active than pure Cu or Cu ultrathin films, especially at potentials more negative than $-0.85$ V versus MSE. The reason for the enhanced activity can be ascribed to H$_{ads}$ atoms accommodated selectively on the Au sites at around $-0.95$ V versus MSE. These atoms are believed to act as reducing agents thus facilitating the entire reaction. Further work focused on identification of products and intermediates of the reaction on Cu–Au ultrathin-film catalysts is planned in the future. Also, DFT calculations would be a necessary addition for further explanation of the mechanism of this phenomenon.

The durability of the studied bimetallic and monometallic catalysts was also tested for up to 92 potential cycles. The Cu$_{0.70}$Au$_{0.30}$ ultrathin film showed better durability than monometallic Cu. A hindered spontaneous Cu dissolution and minimized hydrogen poisoning by adding Au as more noble metal to Cu were both identified as possible reasons for the better durability of alloy/bimetallic catalyst. Finally, studies of the impact of H$^+$ ions on nitrate electroreduction suggested the highest activity in the lowest pH solution of both Cu$_{0.70}$Au$_{0.30}$ and pure Cu film catalysts.

#### 4. EXPERIMENTAL SECTION

##### 4.1. Electrode Preparation

The working electrodes used for all electrochemical and morphological characterization experiments in this work are polycrystalline gold and polycrystalline copper, Au (poly) disks (0.9999 purity) and Cu (poly) of 6 mm diameter and 2 mm thickness. The Au and Cu surface preparation was initiated by mechanical polishing down to 1 μm using water-based, deagglomerated alumina slurry (Buehler). After polishing, Cu electrode was thoroughly rinsed with Barnstead Nanopure water (18.2 MΩ cm). The Au electrodes were immersed in warm concentrated HNO$_3$ to remove any trace contaminants before thorough rinsing with Barnstead Nanopure water (18.2 MΩ cm). The Cu crystals were then annealed to red hot in a propane torch for 5 min before being cooled rapidly in an ultrapure nitrogen atmosphere and finally covered with a droplet of the Barnstead Nanopure water to prevent surface contamination.

##### 4.2. Cell Setup

In the electrochemical cells, the electrodes were immersed and held in a hanging meniscus configuration. All electrochemical experiments were performed in three-electrode setup using solutions made with Barnstead Nanopure water and ultrahigh purity grade chemicals as received from the vendors. A saturated mercury–mercurous...
sulfate electrode with a potential of 0.650 V versus the normal hydrogen electrode was used as reference electrode in most experiments unless stated otherwise in the text. Also, a Pt wire served as the counter electrode (CE) in all experiments. All potentials in the manuscript are presented versus MSE, and all current densities are normalized with respect to the geometric area of the electrode. All electrolytes used in deposition and characterization routines were purged with ultrapure N₂ for at least 30 min before the experiments.

4.3. Characterization of Au Electrodes before and after Deposition. Pb UPD CV was performed on the electrodes to analyze the Au surface and electrochemical surface area development. The Pb UPD solution contained 100 mM NaClO₄ (Sigma, 99.99%), 10 mM HClO₄ (GFS Chemical, 70% redistilled), and 3 mM Pb(ClO₄)₂ (Aldrich, 99.99%). A Pb wire was used as a pseudoreference electrode (PRE), and a Pt wire was used as a counter electrode. Measurements were performed using Princeton Applied Research model 273 potentiostat/galvanostat coupled with CorrWare Software. The same setup and software were used also in all other electrochemical experiments in this work.

4.4. Cu–Au and Pure Cu Ultrathin-Film Growth. The deposition of Cu–Au ultrathin films on polycrystalline Au surface was conducted by SLRR of Pb UPD in a single three-electrode flask. The growth solution containing Y mM Cu(ClO₄)₂·2H₂O (Alfa Aesar, 99.999%), Z mM NaAuCl₄·2H₂O (Premion, 99.99%), 1 mM Pb(ClO₄)₂ (Aldrich, 99.999%), 10 mM HClO₄ (GFS Chemicals, 70% redistilled), and 100 mM NaClO₄ (GFS Chemicals, 98%) was purged with ultrapure N₂ for at least 30 min. Six different solutions with [Cu²⁺]/[AuCl₄⁻] molar ratios of 1:2, 1:1, 2:1, 3:1, 4:1, and 10:1 were used to form Cuₐu⁻Yₐu ultrathin films. For realizing the ratio 1:2, Z was 0.50 mM and Y was 0.25 mM. For all other ratios (starting with 1:1), Y was kept constant at 0.50 mM, whereas the Z was decreasing from 0.50, 0.25, 0.17, 0.13, to 0.05 mM, respectively. The SLRR protocol consisted of repeated steps of Pb UPD formation by a 1 s potential pulse to −0.850 V (vs MSE) followed by a galvanic replacement taking place at open-circuit potential (OCP). The cut-off potentials were −0.25, −0.350, −0.400, −0.415, −0.425, and −0.460 V (vs MSE) at Cu/Au solution ratio of 1:2, 1:1, 2:1, 3:1, 4:1, and 10:1, respectively. A solution containing 0.5 mM Cu(ClO₄)₂, 2H₂O (Alfa Aesar, 99.999%), 1.0 mM Pb(ClO₄)₂ (Aldrich, 99.999%), 10 mM HClO₄ (GFS Chemicals, 70% redistilled), and 100 mM NaClO₄ (GFS Chemicals, 98%) was used for the deposition of pure Cu ultrathin films, as described elsewhere. All deposition experiments were monitored by open-circuit chronopotentiometry carried out with the potentiostat and software mentioned above.

4.5. Cu Anodic Stripping. After deposition, selective stripping of Cu from synthesized Cu–Au ultrathin films was conducted by anodic stripping voltammetry in 1 mM CuSO₄ and 100 mM HClO₄ (GFS Chemical, 70% redistilled). The experiments were performed by running anodic scans from 0.10 to 1.20 V versus Cu/Cu²⁺ PRE at a sweep rate of 1 mV s⁻¹.

4.6. XPS Analysis. XPS results were obtained on a PHI 500 VersaProbe XPS equipped with Ar sputtering gun for surface cleaning and depth profiling. A scanned and focused monochromatic Al Kα X-ray beam was utilized to irradiate elements on the sample surface. The emitted photoelectrons were captured and analyzed by Hemispherical Analyzer with 16 channels. The atomic composition of the prepared Cu–Au thin film was analyzed by binding energy and intensity of the peak.

4.7. Nitrate Electroreduction Testing. After composition analysis, the activities of prepared Cu–Au ultrathin film, polycrystalline Cu, polycrystalline Au, and Cu ultrathin film were tested by running a CV in 10 mM HClO₄ and 10 mM HNO₃ over a potential range from −0.45 to −1.45 V (vs MSE) at a sweep rate 20 mV s⁻¹. A durability test was carried out by the repeating above-described CV process for 92 cycles.

4.8. pH Measurement and Adjustment. OAKTON pH700 was employed to measure the pH of the solution. The pH meter was calibrated by pH 7.00 buffer (Fisher, certified pH 6.99–7.01 @ 25 °C) and pH 4.00 buffer (Fisher, certified pH 3.99–4.01 @ 25 °C). The pH was controlled by tuning the concentration of HClO₄ from 10 to 0.01 mM.
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ACS Omega

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Growth by Surface-Limited Redox Replacement of Cu and H UPD

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