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DOI
10.1002/cctc.202301370

Publication date
2024

Document Version
Final published version

Published in
ChemCatChem

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Citation for published version (APA):

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Enhancing Electrocatalytic Synthesis of Glycine with CuPb_{1ML} Electrode Synthesized via Pb UPD


In the field of reductive organic electrosynthesis, the hydrogen evolution reaction (HER) is considered a parasitic reaction that lowers the Faradaic efficiency of the synthesis. Metals with a high overpotential for HER are often used to prevent this. However, this limits the catalytic materials that can be used in these reactions. To expand upon the scope of available electrocatalysts, we prepared a CuPb electrode via underpotential deposition (UPD). We thereby created an electrocatalyst with a single monolayer of Pb, CuPb_{1ML}, which in Pb weight loading is only 415 ng cm^{-2}, yet its properties could still effectively inhibit HER. The CuPb_{1ML} electrode was used in the electrosynthesis of glycine from oxalic acid and hydroxylamine. This reaction served as a model for a C-N bond forming reaction in acidic aqueous media. The CuPb_{1ML} electrode was compared against a pure Pb and Cu metal electrode. The CuPb_{1ML} electrode showed a Faradaic efficiency for glycine production of 57%, which was 9-fold higher than Cu and rivaled the Pb electrode. The catalytic activity of CuPb_{1ML} was 211 μmol h^{-1} cm^{-2}, which is higher than both Cu and Pb. The mechanism of the electrodereaction was then studied via in situ Fourier Transform Infra-Red (FTIR) spectroscopy. These results hinted to an evolution of the electrocatalyst during the electrolysis reaction, which was then studied via Scanning Electron Microscopy (SEM) and X-Ray Photoelectron spectroscopy (XPS). We found that the Pb monolayer restructured during catalysis, forming microparticles that were active in the reaction based on the listed experiments. Pb alloying into the lattice, which can occur during UPD, also lowered the HER, further facilitating glycine synthesis. Thus, our research also shows how Pb UPD impacts the catalytic properties of a metal both through monolayer deposition as well as surface alloying.

Introduction

The energy transition and the electrification of industrial sectors brings both challenges and opportunities. Organic electrosynthesis is the direct application of electrons for chemical transformations and is an interesting approach to chemical synthesis. It is accomplished by allowing redox transformations to be performed through direct interaction with an electrocatalyst. [1] Because it uses fewer stoichiometric chemical redox reagents, the electrochemical method is safer and cheaper than conventional thermochemistry. [2] In recent years, there has been a surge of interest in electrosynthesis reactions that form a C-N bond. Several interesting transformations are possible here, including the synthesis of simple amines, amino acids, and fertilizers such as urea. [3-7] As a result, making C-N bond containing molecules via electrosynthesis is an interesting process for industrial application.

A comparison of literature studies on electrochemical C-N bond formation reveals that they are often synthesized through electrodereaction in aqueous media. [8-10] Consequently, the hydrogen evolution reaction (HER) is an unwanted side reaction, as it can lower the overall Faradaic efficiency (FE) of the process. [11] Traditionally, when performing electrodereaction in water, proton reduction is avoided by choosing an electrode material with a high HER overpotential. [12] However, this limits the possibility of using metals with interesting electrocatalytic capabilities, as they are often also good catalyst for the HER. [13,14]

Copper electrodes, for example, are interesting since they are effective electrocatalysts both in the CO₂ reduction reaction and in NO₃⁻ reduction. [15,16] Therefore, it is not surprising that C-N bond forming electrodereaction frequently use Cu-based materials. [17-19] The problem with using Cu based catalysts is that Cu can also perform HER, especially when using an acidic electrolyte. [20] In this work, we therefore set out to find a method which allows us to limit the HER of a Cu electrode.
and thereby improve its efficiency in electroreductive C–N bond formation in aqueous acid media.

Our strategy was to deposit a minimum amount of lead (Pb) metal, which has a high overpotential for HER, on a Cu surface. We envisioned this could be achieved by using underpotential deposition (UPD)\(^{(23)}\) of Pb. UPD deposits only a single monolayer on the electrode, which we postulated could already significantly impact the catalytic capabilities of the electrode. To test our hypothesis, we chose the electrosynthesis of glycine as a model reaction. Glycine electrolysersynthesis is performed in acidic aqueous media, which is prone to HER. Glycine itself is a worthy product because it is both a food supplement and an additive for various pharmaceuticals\(^{(22)}\), making it an ideal candidate to test our strategy.

We found that the deposition of a single monolayer of Pb on Cu (CuPb\(_{1\text{ML}}\)) resulted in an efficient electrocatalyst, with high FE for glycine that was comparable to that of a pure Pb electrode. Additionally, the electrocatalytic activity of CuPb\(_{1\text{ML}}\) was greater than both the pure Cu and Pb metals. Further mechanistic study of the CuPb\(_{1\text{ML}}\) electrode was performed using \textit{in situ} Fourier Transform Infra-Red spectroscopy (FTIR), as well as surface analysis by Scanning Electron Microscopy and X-Ray Photoelectron spectroscopy (SEM and XPS) to study the electrocatalyst before, during and after reaction. Our results showed that the Pb monolayer on Cu is highly mobile during electrocatalysis, forming Pb microparticles on the surface, revealing the Cu layer underneath. Further interpretation of these results indicates that the inhibition of HER is not only caused through the deposition of the Pb monolayer, but also due to surface alloying of Pb with Cu metal.

**Results and Discussion**

A Cu electrode with a single lead monolayer was prepared via Pb UPD (herein denoted as CuPb\(_{1\text{ML}}\))\(^{(21)}\). The electrode was then characterized or used as the electrocatalyst in the synthesis of glycine from hydroxylamine and oxalic acid as an electroreductive model reaction\(^{(16)}\).

**CuPb\(_{1\text{ML}}\) electrode preparation and characterization**

The principle of UPD hinges on the unusual phenomenon that some heterometallic bonds are stronger than their homometallic analogues\(^{(23)}\). In this specific example, the Cu–Pb bond is stronger than the Pb–Pb bond. Therefore, one can form Cu–Pb bonds by applying a potential on a Cu electrode that is less negative than the thermodynamic potential for Pb reduction/oxidation. By applying this potential in an electrolyte containing Pb ions, Cu–Pb bonds will be formed until a full monolayer coverage of the electrode is reached, thereby synthesizing a CuPb\(_{1\text{ML}}\) electrode. This principle is further illustrated by a typical CV (Figure 1) where an electropolished Cu electrode is cycled in a 0.2 mM Pb(ClO\(_4\))\(_2\) and 10 mM HClO\(_4\) solution\(^{(24)}\). Following the scan direction, we see first the UPD deposition event (i) at approximately –0.1 V vs. RHE. Subsequently the reduction event at ca. –0.2 V vs. RHE (ii) and its associated oxidation (iii) at –0.15 V vs. RHE show the thermodynamic redox potential of Pb. In agreement with previous reports using Cu single crystals\(^{(23)}\), the UPD stripping peaks are visible at around 0.05 V vs. RHE (iv), which corresponds to the stripping of Pb from Cu(100) sites, whereas the peak at 0.2 V vs. RHE (v) corresponds to the stripping of Pb from Cu(111) sites. After performing the CV, the CuPb\(_{1\text{ML}}\) electrode was synthesized by applying a potential of –0.1 V vs. RHE for 5 minutes.

The stability of the CuPb\(_{1\text{ML}}\) electrode was evaluated via CV. Previous research by Vasilic \textit{et al.} showed that the Pb monolayer on a Cu electrode is susceptible to rapid oxidation at open circuit potential, after which the Pb ions are said to dissolve in the electrolyte\(^{(24)}\). However, Brankovic \textit{et al.} showed that a Pb monolayer can remain stable on a Au substrate electrode under inert conditions\(^{(25)}\). Therefore, to verify the stability of our Pb monolayer, we ran three different measurements. First, a stripping CV was performed in a Pb-free solution under inert conditions (Figure 1 – red line, see also detailed description in SI section 3). The CV showed a retention of both the current profile and the area of the UPD stripping peaks, indicating that removing the electrode from the electrolyte does not change the Pb monolayer. We also studied the influence of O\(_2\) on the freshly prepared CuPb\(_{1\text{ML}}\) electrode using SEM and XPS. SEM images (Figure S1A and S1B) show that after contact with air the electrode remains flat, with no agglomerates, supporting our claim that the Pb monolayer does not restructure upon removal from the electrolyte solution. The XPS data (Figure S1C, S1D and S1E) indicate that Pb is fully oxidized to a native oxide (PbO, with a binding energy (BE) of the Pb 4f\(_{7/2}\) orbital of 138.3 eV\(^{(26)}\)). The Pb content of 1.95 atomic percentage is comparable to other Pb UPD studies\(^{(27)}\). The Pb weight loading was calculated as 415 ng cm\(^{-2}\) (Equation S1 in SI), well below the toxicity requirements\(^{(28)}\). Based on our findings, we concluded that Pb UPD is a suitable method for preparing our CuPb\(_{1\text{ML}}\) electrocatalyst.

![Figure 1. Cyclic voltammogram of a Cu electrode in an aqueous solution containing 0.01 M HClO\(_4\) and 0.2 mM Pb(ClO\(_4\))\(_2\) (Blue line). Stripping cyclic voltammogram of a freshly prepared CuPb\(_{1\text{ML}}\) electrode in an aqueous solution containing 0.01 M HClO\(_4\) (Red line). Cyclic voltammograms were taken at room temperature with a scan rate of 50 mV s\(^{-1}\). Scan direction indicated in figure.](image-url)
Electrochemical measurements

Prior to bulk electrolysis, the CuPb$_{1ML}$ electrode was electrochemically characterized by CV in a blank aqueous 0.1 M H$_2$SO$_4$ solution (Figure 2A). Afterwards, its activity was studied in a 0.1 M H$_2$SO$_4$ aqueous solution containing 0.25 M oxalic acid and 0.25 M hydroxylamine (Figure 2B). The results for Cu and Pb electrodes are also included for comparison.

In the blank solution, the Pb electrode shows a broad anodic peak (i) corresponding to the Pb/PbSO$_4$ redox process at $-0.1$ V vs. RHE and a smaller cathodic peak (ii) at approximately $-0.35$ V vs. RHE that corresponds to the irreversible redox desorption of the PbSO$_4$ layer.$^{[29-31]}$ A slight increase in current density is observed at high negative potential ($\sim -1.0$ V vs. RHE) likely due to HER.$^{[32]}$ Conversely, both the Cu and CuPb$_{1ML}$ electrodes showed an increase in current density at potentials more negative than $-0.4$ V vs. RHE, which was considered to be caused by HER.$^{[33]}$ Surprisingly, even with a Pb monolayer on the Cu surface, hydrogen evolution is not completely suppressed. We only observe a slight shift of approximately 0.1 V towards more negative onset potential when compared to a pure Cu electrode.

Upon adding 0.25 M oxalic acid and 0.25 M hydroxylamine (Figure 2B), all electrodes showed an increase in current density, likely due to the electrochemical reduction of the substrate (oxalic acid).$^{[33]}$ On the Pb electrode, the reductive process occurs at potentials lower than $-0.8$ V vs. RHE, whereas on both Cu and CuPb$_{1ML}$ electrodes, as there is no significant shift in potential, we surmise that hydrogen evolution and electroreductive amiation are competing.

Electrochemical reductive amiation of oxalic acid

The electrocatalytic activity of the CuPb$_{1ML}$ electrode was studied for the electroreductive amiation of oxalic acid with hydroxylamine to glycine as a model reaction. Chronoamperometry measurements were performed at various potentials ranging from $-0.7$ V and $-1.3$ V vs. RHE for 4 hours and the FE and yields are shown in Figure 3A and B, respectively. Previous work using an amalgamated Cu electrode (e.g. Hg alloyed) showed an inverse correlation between the FE and the applied potential.$^{[36]}$ Conversely, our results show that at potentials more negative than $-1.0$ V vs. RHE, the FE towards glycine increases considerably (Figure 3A). The maximum FE of glycine of 57% was reached at $-1.3$ V vs. RHE corresponding to a glycine yield of 48% with a total conversion of oxalic acid of 76% (Figure 3B). These findings demonstrate that the amiation reaction outperforms the competitive HER in this potential range.

The carbon balance is also significantly lower (87%), indicating some unidentified products. In another study, Xian et al. show that the oxime intermediate can decarboxylate in the electrolysesis of amino acids, producing a nitrile product.$^{[34]}$ In our system, this nitrile would be hydrogen cyanide (HCN), which we would not detect with our analysis method. Therefore, to minimize the risk of toxic HCN formation and to maintain the carbon balance, we did not perform chronoamperometry at potentials more negative than $-1.3$ V vs. RHE.

To examine the impact of the Pb monolayer on Cu on the electroreductive amiation performance, we also carried out this reaction using the pure metal electrodes Pb and Cu at the optimized potential of the CuPb$_{1ML}$ electrode at $-1.3$ V vs. RHE (Figure 4). Figure 4A shows the FE of the various products after 4 hours of electrolysis. The CuPb$_{1ML}$ electrodes outperform Cu in terms of FE% for glycine (57% and 9%, respectively), while the FE% of Pb electrode was slightly higher (60%). However, the total glycine formation rate (Figure 4B) was higher on CuPb$_{1ML}$ electrode (211 μmol h$^{-1}$ cm$^{-2}$) than on either Cu (139 μmol h$^{-1}$ cm$^{-2}$) or Pb (114 μmol h$^{-1}$ cm$^{-2}$). This indicates that the CuPb$_{1ML}$ material is an efficient electrolysis catalyst for the electro-amimation reaction, as it produces glycine with high yield and selectivity. The increase in both FE and total glycine formation rate supports the concept that the presence of just one Pb monolayer on Cu is enough to significantly inhibit HER. Finally, the stability of the CuPb$_{1ML}$ electrode was tested over 48 h at $-1.3$ V vs. RHE. Over this period, the FE towards glycine was reduced to 30%. This decline in FE shows that the CuPb$_{1ML}$ electrode has limited stability over long reaction period, never-
theless it opens the possibility to design catalysts which can be further optimized for glycine and other amino acids synthesis.

Mechanistic studies using in situ FTIR

The electroreductive amination of oxalic acid with hydroxylamine on the Cu, Pb and CuPb\textsubscript{1ML} electrodes are examined by using in situ FTIR. With this technique, we can gain insight into the mechanistic differences on each electrode, of which the spectra are shown in Figure 5. A summary of the most important bands is visible in Table 1. Reference spectra measured in 0.1 M H\textsubscript{2}SO\textsubscript{4} are given in SI section 5. By monitoring several FTIR bands as a function of the applied potential, we can determine the production and consumption of the chemical species. The Pb electrode (Figure 5A), shows a small negative band at around 1700 cm\textsuperscript{-1} (C=O stretch from oxalic acid) at potentials more negative than −0.5 V vs RHE. As the potential decreases further, this band disappears, and two positive bands at 1745 cm\textsuperscript{-1} (C=O stretch) and 1238 cm\textsuperscript{-1} (C=O stretch) are formed, which are most likely associated with carbonyl and carboxylic acid groups, respectively\textsuperscript{[25]} These bands indicate the consumption of oxalic acid followed by formation of glyoxylic acid, which is converted to glyoxylic oxime upon reaction with hydroxylamine. At lower potentials, the relative intensity of these bands decrease, and small positive bands appears at 1415 cm\textsuperscript{-1} (C=O stretch) and 1236 cm\textsuperscript{-1} (C=O stretch) (Figure 5A, right inset). We assign these to the CH\textsubscript{2} scissoring and CH\textsubscript{2} waggle vibration of glycine, respectively. At −0.7 V vs. RHE, a positive band appears at 2345 cm\textsuperscript{-1}, associated with the C=O
This is likely due to the decarboxylation reaction of the oxime.\(^{34}\) The appearance of a band at 1623 cm\(^{-1}\) at −0.8 V is related to O–H bending of water, reflecting the instability of the thin layer at more negative potentials due to hydrogen bubble formation.

On Cu and CuPb\(_{1\text{ML}}\) electrodes (Figure 5B and C), from −0.4 V vs. RHE negative bands at 1751 cm\(^{-1}\) (C–O stretch) and 1215 cm\(^{-1}\) (C–O stretch) become visible. These bands reflect oxalic acid consumption. These electrodes also show large positive bands at potentials more negative than −0.5 V vs. RHE.
These bands appear at 1643 cm$^{-1}$, 1565/1573 cm$^{-1}$, 1454 cm$^{-1}$ and 1307 cm$^{-1}$, which correspond to glycinic production. Glycine undergoes significant shifts of IR vibration frequencies upon interaction with a copper surface.\(^{[17]}\) The NH$_2$ scissoring vibration at 1630 cm$^{-1}$ is blue-shifted to 1565/1573 cm$^{-1}$, the CH$_2$ scissoring vibration at 1432 cm$^{-1}$ is red-shifted to 1454 cm$^{-1}$ and the CH$_2$ waggle vibration is red-shifted from 1320 cm$^{-1}$ to 1307 cm$^{-1}$. The band at 1643 cm$^{-1}$ belongs to the NH$_3^+$ asymmetric deformation vibration. This vibration has not shifted, because when the glycine is protonated, it no longer strongly interacts with the copper surface.\(^{[17]}\)

Importantly, we see no CO$_2$ bands, indicating that decarboxylation does not occur on the Cu and CuPb$_{1ML}$ electrodes at the measured potentials (minimum $-0.8 \text{ V vs. RHE}$). In our bulk electrolysis results, the carbon balance only goes below 100% at potentials more negative than $-1.2 \text{ V vs. RHE}$. Due to gas formation during the FTIR measurements, these potentials were not reached. Interestingly, the bands related to glyoxalic acid/oxime (1745 cm$^{-1}$ and 1238 cm$^{-1}$) formation are absent. However, when performing the experiment with only oxalic acid as the substrate (Figure S8), the CuPb$_{1ML}$ electrode does show glyoxal acid formation. This indicates that the latter is converted instantly to glycine in the presence of hydroxylamine.

Based on the in situ FTIR analysis, we assume that glycine has a weak interaction with the Pb surface, as there is only a faint glycine band. The well-defined bands on the Cu and CuPb$_{1ML}$ electrodes suggest a stronger interaction between the substrate and the electrode surface. This similarity was unexpected, given that the blue- and red-shifts that were observed typically indicate an interaction between glycine and the Cu surface. Since the SEM and XPS measurements of a freshly prepared CuPb$_{1ML}$ electrocatalyst reveal no Cu at the surface (vide supra, Figure S1), it would be unlikely that Cu would interact with the substrate. We therefore hypothesize that the CuPb$_{1ML}$ electrode undergoes changes related to the catalyst composition and structure under the reaction conditions, resulting in bare Cu exposed on the surface.

**X-ray Photon-electron Spectroscopy & Scanning Electron Microscopy**

We used SEM and XPS to examine the used CuPb$_{1ML}$ electrode to determine whether the composition and structure of the electrode changed during the reaction. For these measurements, 15 minutes of catalysis was performed at $-1.1 \text{ V vs. RHE}$ with 0.25 M oxalic acid and 0.25 M of hydroxylamine. SEM images of the CuPb$_{1ML}$ surface (Figure 6A, 6B, 6S A and 6S B) show two types of microparticles on the surface, which are present in discrete regions on the electrode. Similarly, XPS shows the presence of two types of Pb species (Figure 6C and 6D), namely PbSO$_4$ (BE of 139.3 eV) and PbO (BE of 138.5 eV). PbSO$_4$ crystals are cubic\(^{[38]}\) and the spherical particles are ascribed to PbO, as spherical PbO particles have been reported.\(^{[39]}\) Therefore we attribute the particles in Figure 6A as PbSO$_4$ and those in Figure 6B as PbO. To quantify the morphological change of the CuPb$_{1ML}$ electrode the roughness factor was calculated before and after catalysis. Electrochemical Impedance Spectroscopy was used, which gave a roughness factor of 1.6 as compared to a pristine CuPb$_{1ML}$ catalyst (SI section 5.0).\(^{[40]}\)

During electrolysis, the PbO monolayer on the surface is reduced to Pb, and then reorganizes to form microparticles. When the electrolysis is stopped, the microparticles re-oxidize upon contact with air. This yields either PbO, or PbSO$_4$ after complexing with SO$_4^{2-}$ ions.\(^{[41]}\) The formation of microparticles exposes bare Cu on the electrode surface during electrolysis explaining the interaction between Cu and the glycine as suggested by the in situ FTIR results. These findings were unexpected since partial coverage of Pb on the surface was expected to give low FE towards glycine, as HER (a facile reaction on Cu in acidic media) would then dominate the electrolysis. This counterintuitive finding prompted us to study the material further, to clarify the factors that cause HER inhibition.

Hochfilzer et al. found that in alkaline media during Pb UPD, the Pb atoms can incorporate into the Cu lattice (in addition to forming a monolayer\(^{[42]}\)). This process is highly irreversible, and the Cu lattice can be restored only through (electro)polishing. We envisioned that in our system a similar process takes place. The lattice Pb atoms could suppress HER even if the Cu surface is not permanently or entirely covered with the Pb monolayer. To test this hypothesis, we synthesized a CuPb$_{1ML}$ electrocatalyst with a surface doping of Pb (see details in SI, section 7). This electrocatalyst was then analyzed via XPS and tested for the same amimation reaction (Figure 7A and B, respectively).

The XPS spectra clearly showed the presence of lead as PbO by the Pb 4f$_{7/2}$ at 138.4 eV (Figure 7A). The Pb 4f$_{7/2}$ peak of the CuPb$_{1ML}$ electrocatalyst appears at a higher binding energy compared to the Pb 4f$_{7/2}$ peak of the CuPb$_{1ML}$. This difference can be attributed to the formation of an alloy in the CuPb$_{1ML}$ Catalyst (see details in SI, section 8).

We then compared performance of this CuPb$_{1ML}$ electrocatalyst to that of Cu and CuPb$_{1ML}$ by performing 4 hours of bulk electrolysis with 0.25 M oxalic acid and 0.25 M hydroxylamine using the standard conditions. The FE towards glycine (18%) and the activity (203 mmol h$^{-1}$ cm$^{-2}$) of the doped electrocatalyst was between that of Cu and CuPb$_{1ML}$. In all electrolytic aspects the CuPb$_{1ML}$ electrocatalyst outperformed Cu, even though the Pb content of this material was much lower than for the CuPb$_{1ML}$ electrocatalyst ($\sim$38 ng cm$^{-2}$ compared to 415 ng cm$^{-2}$ for CuPb$_{1ML}$, see SI section 8). Clearly, both the surface doping of Cu as well as the monolayer deposition play important roles in the inhibition of HER, as well as in promoting the conversion of oxalic acid and hydroxylamine to glycine synthesis. Figure 8 shows a schematic of the development of the electrode surface and the reaction pathway. After a short reaction time, the CuPb$_{1ML}$ electrocatalyst reorganizes to a surface with Pb microparticles which play a role as the active catalytic sites. However, the microparticle formation also...
Figure 6. A, B) SEM imaging of a CuPb\textsubscript{1ML} electrode after catalysis on two different regions of the same electrode (25000x magnification, 2.00 kV accelerating voltage, ETD). C, D) XPS Pb 4f scans of a CuPb\textsubscript{1ML} electrocatalyst after catalysis. Catalysis was performed at −1.1 V vs. RHE for 15 minutes with 0.25 M oxalic acid and 0.25 M hydroxylamine.

Figure 7. A) Pb 4f XPS of the CuPb\textsubscript{doped} electrode. B) Electrolysis results of glycine synthesis for the CuPb\textsubscript{doped} electrode compared to Cu and CuPb\textsubscript{1ML} showing Faradaic efficiency over time with 0.25 M oxalic acid and 0.25 M hydroxylamine in 0.1 M H\textsubscript{2}SO\textsubscript{4} in H\textsubscript{2}O.
CuPb\textsubscript{1ML} electrocatalyst opens exciting opportunities for alternative and more sustainable electrosynthetic procedures normally performed with traditional Pb electrodes.

**Experimental section**

**Electrochemical measurements**

All water used in this research was purified using a Milli-Q Millipore system with a total organic carbon content lower than 3 ppb and a resistivity higher than 18 MΩcm at room temperature. Prior to electrochemical experiments, all glassware was stored overnight in an aqueous 1 g L\textsuperscript{-1} KMnO\textsubscript{4} (VWR chemicals, GPR REACTPUR) and 0.5 M H\textsubscript{2}SO\textsubscript{4} (Sigma-Aldrich, ACS reagent) solution. Before use, traces of KMnO\textsubscript{4} were removed from the glassware by rinsing at least three times with ultrapure water, followed by immersion in a dilute aqueous H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{2}O\textsubscript{2} (1:0.3 M) solution to oxidize organic and KMnO\textsubscript{4} residue. Afterwards, the glassware was boiled in fresh Milli-Q water three times before use.

All electrochemical experiments were performed at room temperature. For cyclic voltammetry (CV), a single compartment three-electrode electrochemical glass cell configuration was filled with 100 mL aqueous 0.1 M H\textsubscript{2}SO\textsubscript{4} solution which was used as the supporting electrolyte. The electrolyte was prepared to have a final concentration of 0.25 M oxalic acid (Sigma-Aldrich, ACS reagent) and/or 0.25 M hydroxylamine sulfate (TCI chemicals, >98.0% purity). Glassy carbon (GC, MaTeck) and a HydroFlex Reversible Hydrogen Electrode (RHE, Gasketel) were used as counter and reference electrodes (CE and RE), respectively. Before electrochemical measurements, the electrolyte was purged with N\textsubscript{2} gas (Linde Gas, 99.999%) for 15 minutes. The working electrodes (WE) used were either a Cu disc (Equilabrium, ø = 5 mm) or Pb disc (Mateck, ø = 5 mm, 99.99%). The Cu electrode was electropolished for 3×10 seconds at 3.0 V vs. a Cu reference/counter electrode in an aqueous 66% (v/v%) H\textsubscript{2}PO\textsubscript{4} solution before use. After electropolishing, the surface of Cu was characterized in a potential range between −0.25 V and 0.45 V vs. RHE in a deaerated 0.1 M NaOH (MaTeck, 99 + %) solution (Figure S13). The Pb electrode was first mechanically polished with a 3.0 μm diamond suspension (Buehler) on a MicroCloth polishing cloth (Buehler), after which it was electropolished in an aqueous 0.5 M H\textsubscript{2}SO\textsubscript{4} solution at −1.8 V vs. Pt reference/counter for 500 seconds. A CV was made in the reaction mixture of 0.25 M oxalic acid and 0.25 M hydroxylamine sulfate in 0.1 M H\textsubscript{2}SO\textsubscript{4} to ensure the removal of all PbOx species (Figure S14). The CuPb electrode containing 1 monolayer of Pb on Cu (CuPb\textsubscript{1ML}) was synthesized as follows: the Cu electrode was prepared as previously described, but after characterizing the electrode surface, UPD\textsuperscript{21} was performed at −0.1 V vs. RHE for 5 minutes in an aqueous electrolyte containing 0.01 M HClO\textsubscript{4} (Acros, ACS reagent) and 0.2 mM PbClO\textsubscript{4} (Sigma-Aldrich, 99.995%). The freshly prepared electrode is either used to confirm successful electrodeposition by performing a stripping CV, or it is used as the WE in the electrochemical procedures.

**Bulk electrolysis**

The preparative scale reactions were performed in a two-compartment electrochemical glass cell configuration divided by a Nafion-117 membrane (FuelCellstore). Each compartment was filled with an aqueous 30 mL 0.1 M H\textsubscript{2}SO\textsubscript{4} solution. 0.25 M oxalic acid and/or 0.25 M hydroxylamine sulfate were added to the catholyte compartment. The anolyte compartment contained a graphite (MaTeck, ø = 6 mm, 1 = 90 mm) CE. The catholyte compartment contained a...
Hydroflex RHE (Gaskatel) and the WE, which was a Pb rod (A \text{surface} = 3.10 \text{ cm}^2, \text{MaTeck}, 99.99\% ), a Cu wire (A \text{surface} = 0.498 \text{ cm}^2, \text{MaTeck}, 99.99\% ), or a CuPb \text{disk} wire (A \text{surface} = 3.76 \text{ cm}^2, \text{MaTeck}, 99.99\% Cu). The WE were pretreated in the same fashion as for the CV experiments (vide supra). The solution was purged with N\text{2} gas (Linde Gas, 99.999\%) for 15 minutes and subsequently kept under inert atmosphere by passing a constant N\text{2} stream over the solution. The electrolysis was performed at the desired potential while stirring at \(\approx 150\) rpm in the catholyte compartment and with an unstirred anolyte compartment, using an Autolab Potentiostat (Metrohm M204). At each time point, three aliquots of 100 \(\mu\)L were taken from the reaction mixture for HPLC analysis (vide infra).

High Performance Liquid Chromatography analysis

Liquid products were detected using a high-performance liquid chromatography (HPLC) Agilent 1260 Infinity II system equipped with an Agilent Technologies Inc. Aminex HPX 87-H column (300x7.8 mm) and a RID and VWD detector. An isocratic chromatography method was used with an eluent of 5 mM H\text{2}SO\text{4} in water and a column temperature of 65 \(\text{°C}\). Aliquots of the reaction mixture (100 \(\mu\)L) were diluted in 900 \(\mu\)L Milli-Q water containing 12.5 \(\mu\)M propionic acid as an internal standard, which has a well-known retention time under the employed conditions. The product yield of oxalic acid, glyoxylic acid and glycolic acid was calculated by fitting the results on a predetermined regression line (Figure S15). Although glyoxylic acid was mostly converted to glyoxylic oxime in the reaction mixture, the column composition was such that the amount of glyoxylic oxime in the HPLC assay was negligible. A derivation method was employed to determine the amount of glycine, as described in literature (Scheme S1). This was done by adding 200 \(\mu\)L of a 1 M KNO\text{3} solution to the samples after the initial HPLC assay, after which the samples were heated to 45 \(\text{°C}\) for 90 minutes in a convection oven. This procedure converted the glycine to glycolic acid. After subtraction of the previously determined concentration of glycolic acid the concentration of glycine in the reaction mixture was accurately determined (Figure S16).

In situ Fourier Transform Infra-Red Spectroscopy

In situ Fourier Transform Infra-Red (FTIR) spectroscopic measurements were performed to provide information about possible intermediates and products of the electrochemical reduction of oxalic acid and hydroxylamine. FTIR spectroscopic measurements were carried out in a Bruker Vertex 80-V IR spectrometer equipped with a liquid nitrogen cooled MCT detector. A Veemam III (PIKE Technologies) was positioned in the spectrometer, wherein a home-made three electrode spectroelectrochemical cell with a CaF\text{2} prism attached to the bottom was placed. A cell was filled with approximately 20 mL of 0.25 M oxalic acid and/or 0.25 M hydroxylamine in 0.1 M H\text{2}SO\text{4} electrolyte. Cu, Pb or CuPb \text{disk} (MaTeck) were used as the WEs, whereas platinum and a home-made reversible hydrogen reference were used as the CE and RE, respectively. The WE was pressed against the CaF\text{2} prism to obtain a thin film configuration. The cell was purged with argon for 15 minutes and subsequently kept under inert atmosphere. FTIR spectra were collected in a range of 4000–1000 \text{cm}^{-1} at a resolution of 8 \text{cm}^{-1} for 100 scans. Spectra were collected over a potential range of 0.1 \text{V} increments from 0.0 \text{V} to \(-1.1\) \text{V} vs. RHE, or until hydrogen evolution deteriorated the quality of the data. The spectra are presented as absorbance, according to A = \(-\log (R/R_0)\), where R and \(R_0\) are the reflectance corresponding to the single beam spectra obtained at the sample and reference potentials, respectively. In these difference spectra, negative bands (pointing down) correspond to the species that were present on or near the electrode surface at the reference potential and that are “consumed” at the sample potential. Positive bands (pointing up) correspond to the formation of species at the sample potential. All the spectro-electrochemical experiments were performed at room temperature.

X-ray Photon-electron Spectroscopy & Scanning Electron Microscopy

The X-ray photoelectron spectroscopy data were acquired using a K-Alpha ultra-high vacuum X-ray photoelectron spectrometer manufactured by ThermoFisher Scientific. This instrument was equipped with a monochromatic aluminum anode (\(K\alpha = 1486.68 \text{ eV}, 72 \text{ W}\)) X-ray source featuring a spot size of 400 \(\mu\)m. The detection system comprised a 180° double focusing hemispherical analyzer with a 128-channel detector. During the measurements, the samples were subjected to a pass energy of 50 eV. The survey spectra were employed to ascertain the elemental composition of the samples. The elements detected were copper, lead, oxygen, and carbon. To assess the charging states of the elements of interest, we examined the core-level lines Cu 1s, O 1s, Cu 2p, Cu 2p, and Pb 4f. Subsequently, the acquired spectra underwent processing using CasaXPS software. To calibrate the binding energy scale, the binding energy of Cu 1s was set to 932.83 eV. For the XPS spectra analysis, a Shirley background was employed, and the curve fitting process utilized a Gaussian function GL (30) for Cu 2p and a Laurenzian asymmetric function LA (1.53, 243) for Pb 4f. In particular, the Cu 2p \text{spectra} (\text{RF} = 18.1471) were fitted by applying a peak area constraint for Cu 2p that was 1.36 times larger than the shake-up peak. An additional peak was introduced to account for the asymmetry of Cu 2p. The constraints for this additional peak were consistent, with the position set 1.4 eV higher than the main Cu 2p peak, and the full width at half maximum (FWHM) was adjusted to Cu 2p that was 1.36 times larger than the shake-up peak. An additional peak was introduced to account for the asymmetry of Cu 2p. The constraints for this additional peak were consistent, with the position set 1.4 eV higher than the main Cu 2p peak, and the full width at half maximum (FWHM) was adjusted to Cu 2p that was 1.36 times larger than the shake-up peak.

Scanning electron microscopy (SEM) analysis of the CuPb \text{disks} electrodes were conducted on a ThermoFisher Apreo S electron microscope with an accelerating voltage of 2 \text{kV} and a 0.20 \text{nA} beam current. Everhart-Thornley and in-column detectors were used for imaging. Images were collected with a resolution of 1536x1024 and a pixel dwell time of 20–25 \text{µs}. SEM and XPS analysis was conducted on both a freshly prepared CuPb \text{disks} electrode and after catalysis at \(-1.1\) \text{V} vs. RHE for 15 minutes with 0.1 M H\text{2}SO\text{4}, 0.25 M oxalic acid and 0.25 M hydroxylamine.

Supporting Information

The authors have cited additional references within the Supporting Information.

Acknowledgements

The research was carried out under project numbers ECCM.T.ECCM.008 and ECCM.TT.MVITU.005. Both research projects were conducted on a ThermoFisher Apreo S electron microscope with an accelerating voltage of 2 \text{kV} and a 0.20 \text{nA} beam current. Everhart-Thornley and in-column detectors were used for imaging. Images were collected with a resolution of 1536x1024 and a pixel dwell time of 20–25 \text{µs}. SEM and XPS analysis was conducted on both a freshly prepared CuPb \text{disks} electrode and after catalysis at \(-1.1\) \text{V} vs. RHE for 15 minutes with 0.1 M H\text{2}SO\text{4}, 0.25 M oxalic acid and 0.25 M hydroxylamine.
Conflict of Interests
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Catalysis • C–N bond formation • Lead monolayer • Organic electrolys thesis • Underpotential deposition