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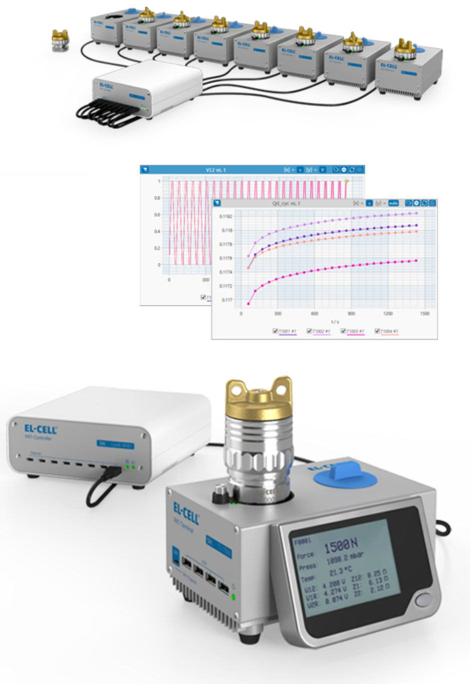

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Copper (II)–Lactate Complexes in Cu_2O Electrodeposition Baths: Stability of the Complexes and Aging of the Baths

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The electrodeposition of Cu_2O, represented by the reaction $2Cu(II) + 2OH^- + 2e \rightarrow Cu_2O + H_2O$ in alkaline baths containing concentrated lactic acid (approximately 3 mol dm^{-3}) as ligands, has been widely studied. In a previous study, such baths were found to generate the complexes $[Cu(H_{-1}L)L]^-$ and $[Cu(H_{-1}L)_2]^{2-}$ (where $L^- = CH_3CH(OH)COO^-$ and $H_{-1}L^- = CH_3CH(O^-)COO^-$) in a manner dependent on the bath pH in the alkaline region. This work first assessed the stability of these Cu(II)-lactate complexes based on computational chemistry. The formation of these complexes typically requires approximately one day to reach thermodynamic equilibrium, suggesting that other kinetically favorable, metastable complexes may form prior to the equilibrium complexes. Based on titration curves, $[CuL_2(HL)]^0$ was identified as the most likely such intermediate and the effect of this complex on deposition orientation was examined. Electrodeposited Cu_2O obtained from a bath not yet at equilibrium with a pH of approximately 9.5 was randomly oriented whereas deposits from an equilibrated bath showed a preferential ⟨100⟩ orientation. These findings suggest that bath aging is an essential step in achieving reproducible Cu_2O electrodeposition. Additionally, modifying the bath preparation method was found to prevent the formation of metastable complexes.

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Thin films of cuprous oxide (Cu_2O; copper(I) oxide), a p-type semiconductor, have received significant attention as possible photocathodes for hydrogen production or light-absorbing layers in solar cells.[1–4] Electrodeposition has proven to be an effective approach to producing such films. Since the pioneering work of Rakhshani et al. in the late 1980s, studies related to the electrodeposition of Cu_2O thin films have typically used alkaline aqueous solutions containing approximately 3.0 M lactic acid as a ligand for Cu(II).[4–7] This electrodeposition reaction is represented by Eq. 1.

$$2Cu(II) + 2OH^- + 2e \rightarrow Cu_2O + H_2O \qquad [1]$$

In general, during various electrodeposition processes, metal complex(es) formed in the electrolyte baths will affect the reduction of metal ions and thus play a critical role in defining the physical properties of the resulting films, and the same is true for the Cu_2O electrodeposition in alkaline baths containing concentrated lactic acid. In particular, it has been observed that the crystallographic orientation of Cu_2O thin films will affect both the extent of photoelectric conversion and photocatalytic performance, making control over orientation essential.[8–10] Even so, the specific complexes that are generated in Cu_2O thin film deposition baths remain unidentified.

In prior work, the authors used a pH titration method that had been modified to account for the time required for complex formation to reach equilibrium, referred to as the "revised pH titration" technique in an earlier paper by the author.[11] The data from this previous research (Fig. 1) indicated that each Cu(II)-lactate complex, $[CuL_2]^0$, had acquired two equivalents of OH^- when the titration reached completion, meaning that the complex $[Cu(H_{-1}L)_2]^{2-}$ was present at equilibrium.[11] Here, $[H_{-1}L]^{2-}$ denotes a lactate ion, $L^- = CH_3CH(OH)COO^-$, that has lost a second proton from the standalone hydroxy group. Data obtained from visible absorption spectroscopy also suggested the formation of an intermediate species, $[Cu(H_{-1}L)L]^-$, during the transition from $[CuL_2]$ to the fully deprotonated $[Cu(H_{-1}L)_2]^{2-}$ complex. Probe electrospray ionization mass spectrometry provided further evidence for the formation of complexes with deprotonated lactate ligands, specifically $[Cu(H_{-1}L)L]^-$ and $[Cu(H_{-1}L)_2]^{2-}$.[11] A multivariate analysis of the visible absorption spectra (electronic spectra) was used to determine the formation constants for these two complexes and to generate complex formation curves and potential-pH diagrams.[12]

The deposition behavior of Cu_2O with lactate ligands and the properties of the resulting product, specifically the orientation and semiconductor properties, are known to be affected by the pH of the alkaline bath, especially in the vicinity of pH 9.[5–7,13–15] However, the underlying mechanism for these differences remains unclear. Previous work by the authors reexamined the electrodeposition behavior of Cu_2O by conducting a series of depositions at precisely controlled cathodic overpotentials to generate potential-pH diagrams.[16] The results suggested that variations in the electrodeposition behavior and in the properties of the deposited material could likely be ascribed to the pH of the bath, which determined whether $[Cu(H_{-1}L)L]^-$ or $[Cu(H_{-1}L)_2]^{2-}$ was the primary species. From these results it was evident that the electrodeposition mechanism can be more effectively understood by considering the effect of pH on the distribution of complexes. Consequently, a rigorous analysis of the complexes present in an electrodeposition bath is a useful approach to both understanding and optimizing the electrodeposition process.

In a Cu_2O electrodeposition bath incorporating lactate ligands, Cu(II) complexes with deprotonated lactate ions are generated across a wide range of pH values in the alkaline region. In general, simple hydroxy groups are not prone to proton loss at mildly alkaline pH values, given the high pK_a values for these groups (15 or above).[17] As an example, the pK_a of the lactic acid hydroxy group is 15.1.[18] However, in these electrodeposition systems, the hydroxy group can deprotonate as a consequence of coordination of this group with Cu^{2+} ions acting as Lewis acids. Evidence for this phenomenon is provided by titration curves, which demonstrate that only hydroxy groups coordinated to Cu^{2+} ions undergo proton loss. In contrast, no proton dissociation is observed from the hydroxy groups of free lactate ions.

The present study used computational chemistry to confirm that hydroxy groups coordinated with Cu^{2+} ions lose protons more readily. Subsequently, the relative probabilities of the formation of

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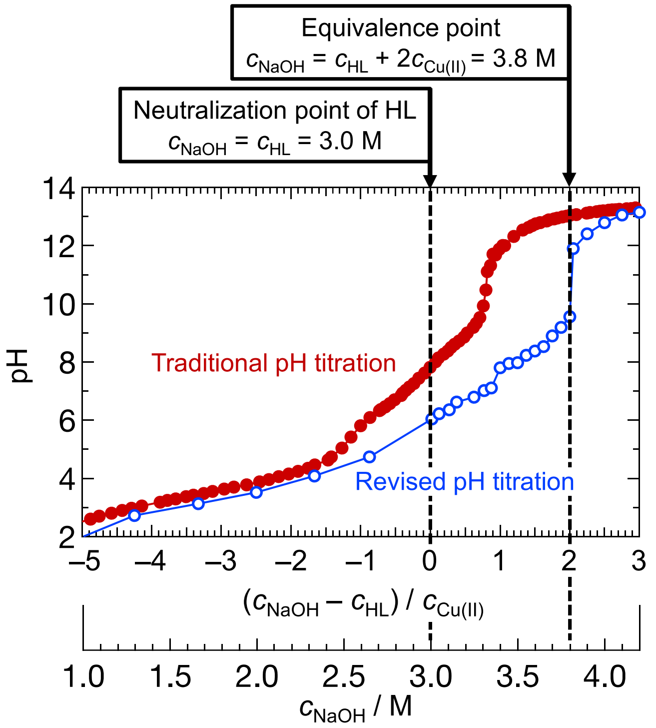

Figure 1. Titration curves for an aqueous 0.4 M copper(II)/3.0 M lactate solution with added NaOH. The dashed lines indicate neutralization and equivalence points. The plots corresponding to traditional and revised pH titrations are depicted in red and blue, respectively. (The titration data was reproduced from Ref. 11).

$[Cu(H_{-1}L)L]^-$ and $[Cu(H_{-1}L)_2]^{2-}$ complexes were ascertained by comparing the complexes, which are otherwise indistinguishable in terms of pH-metry. The data from modified pH titrations and time-dependent visible absorption spectra indicate that $[Cu(H_{-1}L)L]^-$ and $[Cu(H_{-1}L)_2]^{2-}$ require approximately one day to reach thermodynamic equilibrium. This observation implies the initial formation of a kinetically favored metastable complex that subsequently transforms into these more thermodynamically stable complexes over this time span. Identifying these transient complexes is important. Given that the particular complexes in the electrodeposition bath can affect the product characteristics, deposition from a bath that has not reached thermodynamic stability might yield suboptimal products.

Izaki's group, which has studied Cu_2O deposition and solar cells based on Cu_2O,[7,13] has found that it is preferable to carry out deposition after the bath has aged for approximately one day (private communication). Other researchers have noted that the poor reproducibility of Cu_2O deposition experiments may be due to insufficient aging of the bath. In the work reported herein, the kinetically favorable complex noted above was investigated. The orientation of Cu_2O films produced via the electrodeposition in a bath prior to the $[Cu(H_{-1}L)L]^-$ and $[Cu(H_{-1}L)_2]^{2-}$ complexes achieving formation equilibrium was also examined. This study demonstrates an effective approach to avoiding the slow formation dynamics of $[Cu(H_{-1}L)L]^-$ and $[Cu(H_{-1}L)_2]^{2-}$ complexes.

Experimental

Electrochemical deposition.—All electrolytes were prepared with reagent-grade chemicals purchased from Nacalai Tesque and using deionized water (18 MΩ cm) obtained from a Milli-Q system. The copper(II) lactate electrolytes having different pH values employed for the purpose of Cu_2O electrodeposition in this work each contained 0.4 M (M = mol dm^{-3}) copper(II) acetate monohydrate ($Cu(CH_3COO)_2{\cdot}H_2O$) and 3.0 M lactic acid ($CH_3CH(OH)COOH$). The working electrode was made of fluorine-doped tin oxide (FTO, 10 Ω sq.$^{-1}$ resistance, Type VU, 10 mm × 10 mm electrodeposition area, AGC), while the counter electrode was made of Pt. A Ag/AgCl reference electrode (3.33 M KCl, HORIBA) was connected to the electrodeposition bath through an agar salt bridge and employed as the reference electrode. The working and reference electrodes were positioned as close as possible to one another and connected to an electrochemical measurement device (SP-50, Bio-Logic Science Instruments). The electrodeposition bath was not stirred and was held at 40 °C. Each electrodeposition potential was set at a cathodic overpotential of 0.5 V, determined with respect to the equilibrium potential of Cu(II)/Cu_2O in the potential–pH diagram reported in a previous study (see Fig. S1).[12] The electrodeposited materials were washed with deionized water and dried prior to characterization.

Density functional theory calculations.—Density functional theory (DFT) calculations were performed using the general purpose quantum chemical calculation program Gaussian 16 W. The initial molecular structure was generated in the Z-matrix format and verified using GaussView 6.0.16. All calculations employed the LanL2DZ basis set for Cu atoms and the 6–311 G++(d,p) basis set for C, H and O atoms. Structural optimizations were performed with the B3LYP functional (Becke, three-parameter, Lee-Yang-Parr). Solvent effects were considered using the IEF-PCM (Integral equation Formalism Polarizable Continuum Model) approach with water (dielectric constant 78.3553) as the solvent.

Visible absorption spectroscopy.—Visible absorption spectra were recorded using a V-770 spectrophotometer (JASCO) with a halogen lamp. All sample solutions were analyzed over the range of 550–850 nm with a resolution of 0.5 nm and a scan rate of 200 nm min^{-1}. A 1 mm path length quartz cell with a lid was used to acquire spectra of the copper(II)-lactic acid solutions due to the dark color of these solutions. All absorbance data were found to obey the Lambert-Beer law and so could be used to calculate molar absorbance coefficients in units of L mol^{-1} cm^{-1}.

Characterization of Cu_2O deposits.—X-ray diffraction (XRD) patterns were acquired using a RINT2200 instrument (RIGAKU). The $2\theta/\theta$ method was utilized over the range from 20° to 70° with a sampling width of 0.02° and a scanning speed of 1° min^{-1}. The widths of the divergence, scattering and receiving slits were set to 1°, 1° and 0.3 mm, respectively. Cu-Kα radiation was employed (λ = 0.070926 nm) with a tube voltage of 40 kV and tube current of 30 mA. The surface morphologies of deposits were examined using field emission scanning electron microscopy (FE-SEM) with a JEOL JSM-6500F instrument operating at an acceleration voltage of 15 kV. Secondary electron images were acquired.

Results and Discussion

Validation of complex structures by DFT calculations.—Prior studies by the authors suggested that $[Cu(H_{-1}L)L]^-$ and $[Cu(H_{-1}L)_2]^{2-}$ complexes are formed in alkaline solutions.[11] To confirm this, theoretical calculations were performed based on first-principles, beginning with $[CuL_2(H_2O)_2]^0$ (the $[CuL_2]^0$ complex), in which two water molecules are axially coordinated to the complex. Subsequently, the energies of complexes in which either the proton from the lactate ion's hydroxy group or the proton from one of the axially coordinated water molecules (that is, those not attached to the lactate ligand) was dissociated. This enabled a comparison of two complexes that are indistinguishable in pH-metry as a means of determining the lower-energy configuration. In essence, these theoretical calculations identified the proton in $[CuL_2(H_2O)_2]^0$ most likely to be lost and the associated deprotonation energy.

Comparisons of the energy values determined for the $[Cu(H_{-1}L)L(H_2O)_2]^-$ and $[CuL_2(OH)(H_2O)]^-$ complexes, both resulting from the loss of a single proton from $[CuL_2(H_2O)_2]^0$, demonstrated that the value for $[Cu(H_{-1}L)L(H_2O)_2]^-$ should be

21.9 kJ mol^{-1} lower. As such, this product would be thermodynamically more stable (Fig. 2a). An analysis of $[Cu(H_{-1}L)_2(H_2O)_2]^{2-}$, $[Cu(H_{-1}L)L(OH)(H_2O)]^{2-}$ and $[CuL_2(OH)_2]^{2-}$, all of which are the result of the loss of two protons from $[CuL_2(H_2O)_2]^0$, showed energy differences of 44.9 and 42.2 kJ mol^{-1}, respectively (Fig. 2b). These results indicate that the products resulting from proton dissociation from a hydroxy group, $[Cu(H_{-1}L)L(H_2O)_2]^-$ and $[Cu(H_{-1}L)_2(H_2O)_2]^{2-}$, are energetically favored over other species that are indistinguishable in pH-metry. This suggests that such products are thermodynamically more stable, in agreement with prior studies. Hence, $[Cu(H_{-1}L)L]^-$ and $[Cu(H_{-1}L)_2]^{2-}$ would be expected to appear in alkaline solutions, consistent with previous observations.

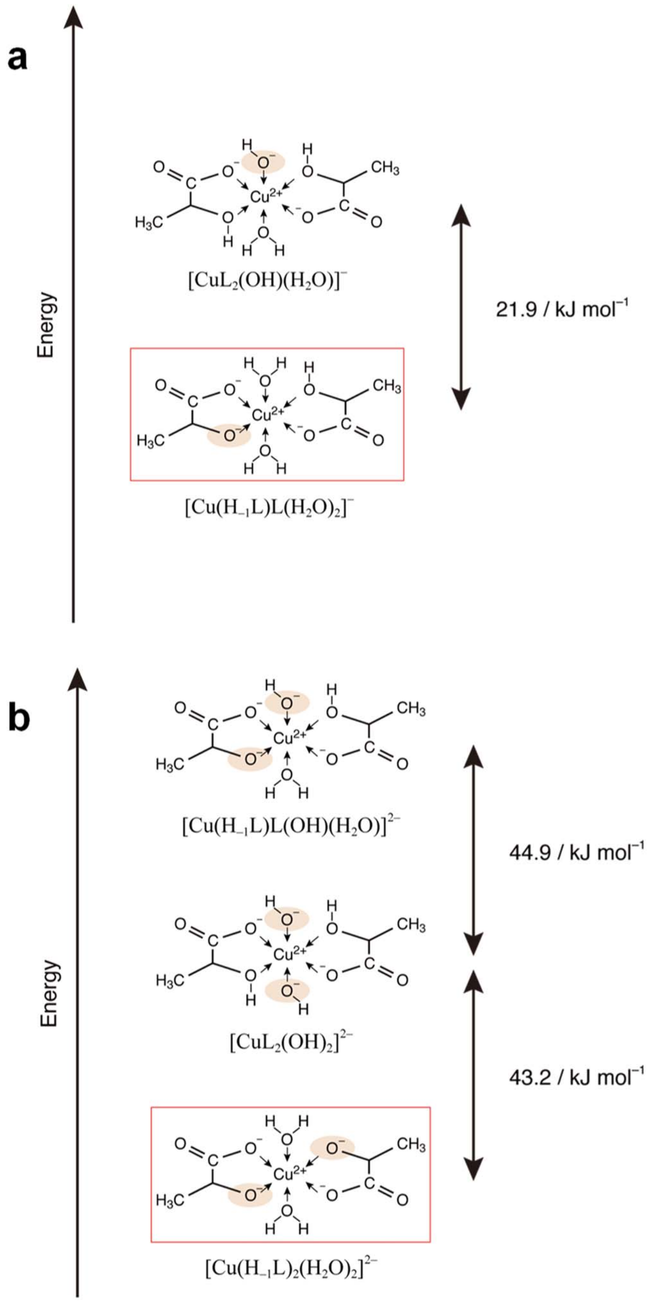

Figure 2. Structures and energy differences of (a) a complex with one proton dissociated and (b) complexes with two protons dissociated from $[CuL_2(H_2O)_2]^0$.

The structure of the kinetically favorable complex.—The kinetically favorable complex described above was assumed to comprise $[CuL_2(HL)]^0$, in which an additional lactic acid (HL) is coordinated to $[CuL_2]^0$ without deprotonation of the acid. The results of the modified pH titration first reported in a previous paper are reproduced in Fig. 1 to explain why the kinetically favorable complex is considered to be $[CuL_2(HL)]^0$. In this modified technique, 30 15 ml aliquots of solutions containing 0.4 M copper(II) and 3.0 M lactic acid were prepared, after which a specific amount of NaOH (97%, Nacalai Tesque) was added to adjust the pH of each sample. These samples were then stored in 20 ml sealed screw-top tubes for one week to allow the complexation process to go to completion.

Upon comparing the data obtained using a traditional pH titration method (that is, adding titrant from a burette to the analyte in a beaker) with those from the revised titration method, it was observed that the titration curves began to diverge at approximately pH 4.5. Notably, this divergence occurred at c_{NaOH} values below 3.0 M, which was the concentration at which all lactic acid was neutralized and the pH was shifted to higher values. Additionally, the final abrupt increase in the titration curve, representing the endpoint, appeared at a c_{NaOH} value of approximately 3.4 M. This result indicates that the NaOH concentration at the endpoint was underestimated by the traditional titration method compared with the actual concentration at complete equilibrium as found using the revised titration procedure. It is apparent that, in the case of the traditional pH titration, all lactic acid in the solution was in the completely unneutralized state (that is, in the form of unprotonated HL with an equal number of moles of Cu^{2+}) at the apparent endpoint. According to the literature, the pK_a of lactic acid is 3.86,[19] meaning that, at the pH of approximately 4.5 at which the plots began to diverge, 18.6% of the total lactic acid may be in the form of neutral (free) HL. The unprotonated HL is presumably stabilized at this point via coordination with the Cu^{2+} ions such that the HL coordinated in this manner does not undergo further proton dissociation up to the apparent endpoint.

At this point it is helpful to consider the complexes that can be formed as a consequence of the coordination of Cu(II) with non-proton-dissociated HLs. Possible candidates include $[Cu(HL)L]^+$ and $[Cu(HL)_2]^{2+}$, each with two lactate ions, or $[CuL_2(HL)]^0$, $[CuL(HL)_2]^+$ and $[Cu(HL)_3]^{2+}$, each with three lactate ligands. The latter complexes have been reported to form in dilute aqueous solutions.[20] However, given that $[CuL_2]^0$, which contains two coordinated L^- ligands, is the most thermodynamically stable complex in the vicinity of pH 4.5, it is unlikely that complexes formed by further titration would be $[Cu(HL)L]^+$, $[Cu(HL)_2]^{2+}$, $[CuL(HL)_2]^+$ or $Cu(HL)_3{}^{2+}$. Therefore, $[CuL_2(HL)]^0$ is presumably the sole kinetically favorable complex. This finding explains the changes observed in the bath after it has been prepared. As shown in Fig. 3, a decrease in pH and a red-shift of the *d–d* absorption band from approximately 660 to 680 nm were observed during the one-day aging period. The former effect reflects proton release associated with the transition of $[CuL_2(HL)]^0$ to $[Cu(H_{-1}L)L]^-$. This can be summarized by the equation

$$[CuL_2(HL)]^0 \rightarrow [Cu(H_{-1}L)L]^- + L^- + 2H^+. \qquad [2]$$

The latter effect occurs because this transition reduces the number of chelating ligands from three to two, thereby weakening the ligand field. $[CuL_2(HL)]^0$ is more likely to be present than $[Cu(H_{-1}L)L]^-$ and, although the precise reason for this remains unclear, it might be related to the minimal dissociation of the standalone hydroxy group. The loss of a proton as part of the path from $[CuL_2(HL)]^0$ to the most stable complex $[Cu(H_{-1}L)L]^-$ is expected to proceed through intermediate states. There are two possible routes for this process. In one, $[CuL_3]^-$ or $[Cu(H_{-1}L)L_2]^{2-}$ is first generated, from which L^- dissociates, leading to $[Cu(H_{-1}L)L]^-$. In the other, an HL ligand is lost from $[CuL_2(HL)]^0$ to give $[CuL_2]$, from which a proton dissociates to

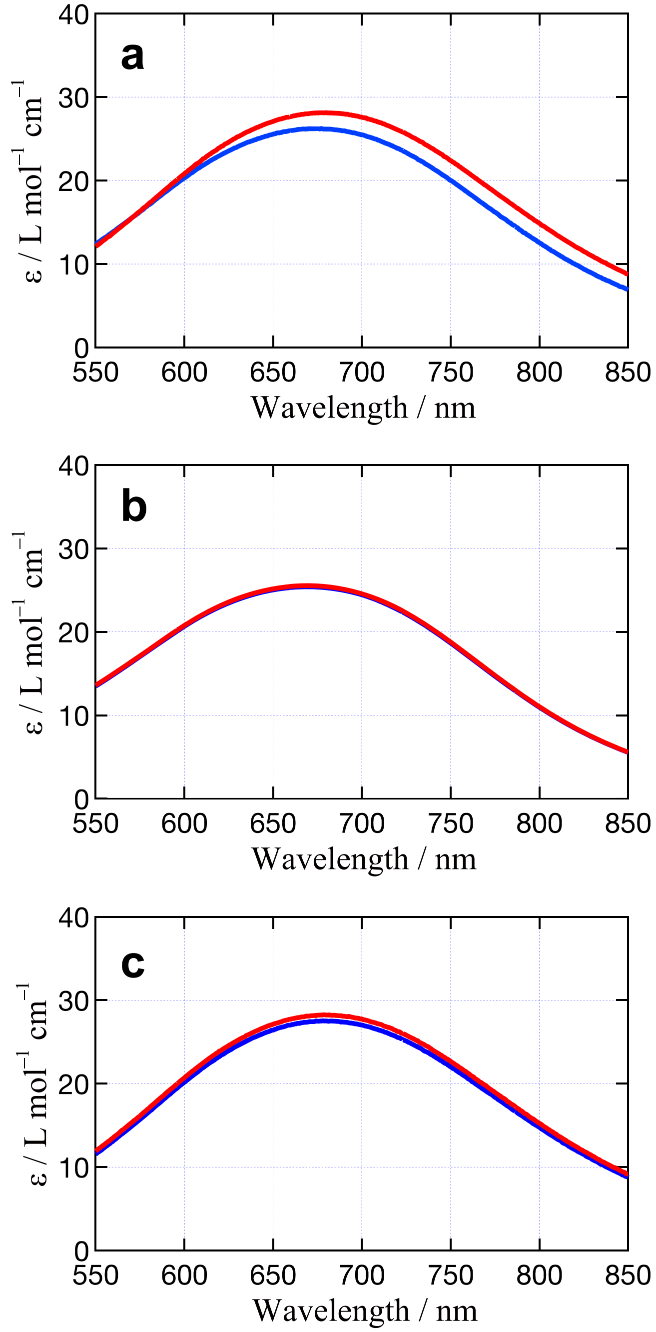

Figure 3. Visible absorption spectra of Cu_2O electrodeposition baths having (a) $c_{NaOH} = 3.8$ M and (b) $c_{NaOH} = 4.0$ M and (c) prepared by adding an excess of sodium hydroxide ($c_{NaOH} = 4.0$ M) followed by 0.3 M acetic acid to partially neutralize the sodium hydroxide. The blue and red lines indicate values immediately after preparation of the bath and after reaching thermodynamic equilibrium following aging of the bath for one day, respectively.

produce $[Cu(H_{-1}L)L]^-$. The determination of the most likely route is beyond the scope of this work and has not been examined in detail.

Cu_2O deposits obtained in the presence of kinetically favorable complexes.—Previous studies have demonstrated that the orientation and semiconductor properties of electrodeposited Cu_2O vary with the pH of the electrodeposition bath.[5–7,13–15] As discussed in the Introduction, these correlations can be explained by variations in the complexes present in the bath.[16] In prior work, electrodeposition was performed in baths that had been allowed to age for at least 24 h to ensure complete equilibration. In contrast, the present study examined the effect of the kinetically favorable complexes on the resulting Cu_2O deposits. This research involved the preparation of aqueous solutions containing 0.4 M copper acetate and 3.0 M lactic acid together with the addition of sodium hydroxide to provide c_{NaOH} values of 3.8 or 4.0 M. Based on the titration data in Fig. 1, the complexes in the bath with $c_{NaOH} = 3.8$ M were expected to change over time shortly after the bath was prepared.

The c_{NaOH} value of 4.0 M exceeded that at the equivalence point at which the $[Cu(H_{-1}L)_2]^{2-}$ complex will form. Hence, it was expected that the complexes in the bath would remain stable and not change over time. The visible absorption spectra of baths with c_{NaOH} values of 3.8 and 4.0 M were acquired both immediately after preparation and after one day of aging. The spectra for the $c_{NaOH} =$ 4.0 sample did not change over time (Fig. 3). In contrast, the spectra acquired with $c_{NaOH} = 3.8$ M exhibited a red shift during aging, as expected, with a concurrent change in pH from 9.8 to 9.5 over one day. In light of the above, we selected two types of baths, both with $c_{NaOH} = 3.8$ M, that were used to assess Cu_2O electrodeposition. One was used immediately after preparation and one was aged for one day to allow equilibration. The trials with these baths used a cathodic overpotential of 0.5 V for electrodeposition with reference to the equilibrium potential of Cu(II)/Cu_2O in the potential–pH diagram obtained in a previous study (See Fig. S1).[12] The electrodepositions were carried out with a charge of 0.5 C cm^{-2}. Figures S2 and S3 show the cathodic polarization curves and chronoamperograms of the electrochemical bath with $c_{NaOH} = 3.8$ M. The shape of the polarization curves are consistent with those previously reported for similar electrolytes.[21,22] After one day of aging, at a bath pH of 9.5, the steady-state current density for electrodeposition was approximately -0.10 to -0.15 mA cm^{-2}.

Figure 4a presents the XRD patterns obtained from the resulting Cu_2O specimens. The bath employed immediately after preparation provided randomly oriented Cu_2O whereas material exhibiting preferential $\langle 100 \rangle$ orientation was deposited from the bath in the equilibrium state. This change in the orientation of the Cu_2O deposits as a consequence of the aging of the bath was confirmed by visible absorption spectra. Previous studies have shown that a preferential $\langle 100 \rangle$ orientation is obtained at pH values $\leqslant 9.4$ while a preferential $\langle 111 \rangle$ orientation appears at pH $\geqslant 9.9$, with the transition between the two orientations occurring in this pH range.[16] The pH of the $c_{NaOH} = 3.8$ M bath was found to be 9.8 immediately after preparation but decreased to 9.5 after one day. This finding suggests that the observed change in orientation with bath aging reflected either changes in the nature of the complexes in the bath or was a result of the variation in pH.

Figures 4b and 4c present surface FE-SEM images of Cu_2O specimens electrodeposited from the bath used immediately after preparation and from the equilibrated bath. The former material exhibits a crystal structure with no distinct growth direction. The complex composition of the fresh bath is believed to have changed dynamically over time, resulting in a lack of a clear growth direction and a random orientation, both of which would be expected to make reproducible Cu_2O deposition challenging. In other words, the use of a less stable pre-aged bath can result in rapid and/or uncontrolled nucleation, leading to random orientations. Conversely, the latter material comprised pyramidal grains surrounded by $\{111\}$ facets that had grown in the $\langle 100 \rangle$ direction perpendicular to the substrate. Based on the above results, the characteristics of Cu_2O deposited at $c_{NaOH} = 3.8$ M may vary, resulting in unstable electrodeposition. This issue can arise with any bath that undergoes changes over time, not only at $c_{NaOH} = 3.8$ M.

A novel bath preparation method for reproducible Cu_2O electrodeposition.—The experimental results of this work indicate that stable Cu_2O electrodeposition requires aging the bath until the kinetically stable complex transitions to a thermodynamically stable complex, after which electrodeposition can proceed in an

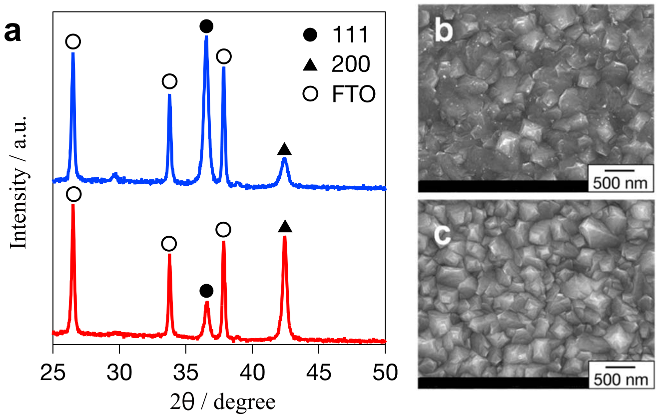

Figure 4. (a) XRD patterns and (b), (c) SEM images of Cu_2O obtained from the electrodeposition bath with $c_{NaOH} = 3.8$ M. These data confirm that Cu_2O was obtained immediately after preparation of the bath (blue, b) and after thermodynamic equilibration following aging for one day (red, c). Each scale bar indicates 500 nm.

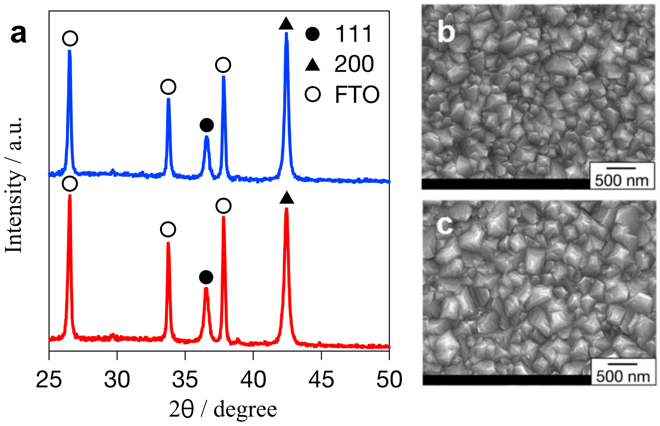

Figure 5. (a) XRD patterns and (b), (c) SEM images of Cu_2O obtained from the electrodeposition bath prepared by adding an excess of sodium hydroxide ($c_{NaOH} = 4.0$ M) followed by partial neutralization using 0.3 M acetic acid. These data confirm that Cu_2O was obtained immediately after preparation of the bath (blue, b) and after reaching the thermodynamic equilibrium through 24 h aging of the bath (red, c). Each scale bar indicates 500 nm.

equilibrium state. However, if kinetically favorable complexes could be avoided such that thermodynamically stable complexes are formed immediately, bath aging would be unnecessary. To prevent the formation of kinetically favorable complexes, a bath preparation process was devised based on adding an excess of sodium hydroxide ($c_{NaOH} = 4.0$ M) followed by the further addition of 0.3 M acetic acid to partially neutralize the sodium hydroxide, resulting in the concentration corresponding to $c_{NaOH} = 3.7$. The initial high OH^- concentration was expected to bypass the formation of kinetically favorable intermediate complexes to promote the formation of $[Cu(H_{-1}L)_2]^{2-}$. Subsequently lowering the pH with acetic acid was intended to ensure the rapid formation of $[Cu(H_{-1}L)L]^-$. The pH value was 13.2 when the bath contained $c_{NaOH} = 4.0$ M, and the final pH value was 9.5 after adding acetic acid.

Figure 5 presents XRD patterns and SEM images for the electrodeposited materials obtained from this bath. The Cu_2O generated in the bath immediately after preparation and that obtained after aging the bath for one day both showed a preferential ⟨100⟩ orientation. In both cases, quadrangular pyramidal grains were grown, similar to the Cu_2O obtained from the equilibrated bath at $c_{NaOH} = 3.8$ M. Additionally, the visible absorption spectrum of this bath was unchanged after aging for one day (Fig. 3c). These results demonstrate that modifying the bath preparation method to prevent the formation of kinetically favorable complexes allowed reproducible Cu_2O electrodeposition without the need for bath aging, which is currently thought to be necessary.

Conclusions

Previous research has identified the complexes $[Cu(H_{-1}L)L]^-$ and $[Cu(H_{-1}L)_2]^{2-}$ as being dominant in alkaline solutions.[11] The present study used computational chemistry to confirm that hydroxy groups coordinated with Cu^{2+} ions dissociate more readily. In addition, the relative probabilities of the formation of $[Cu(H_{-1}L)L]^-$ and $[Cu(H_{-1}L)_2]^{2-}$ were assessed by comparing indistinguishable complexes in terms of pH-metry. The results indicate that these two complexes are indeed prevalent at alkaline pH values.

The generation of these complexes in conjunction with thermodynamic equilibration was found to require approximately one day. In the present study, the complex $[CuL_2(HL)]^0$ was proposed as being kinetically favored in the electrodeposition bath. Cu_2O deposited immediately after bath preparation with an OH^- concentration of 3.8 M, at which point $[Cu(H_{-1}L)L]^-$ or $[Cu(H_{-1}L)_2]^{2-}$ had not yet reached equilibrium, was found to comprise randomly oriented crystals. The same electrodeposition bath after equilibration provided Cu_2O displaying a preferential ⟨100⟩ orientation. Hence, reproducible Cu_2O electrodeposition appeared to require aging of the bath for approximately one day to ensure thermodynamic equilibrium. Modifying the bath preparation method generated Cu_2O having the same orientation as that obtained from the equilibrated bath without the need for bath aging. This work provides important insights into approaches to reproducibly achieving a uniform Cu_2O orientation. This study also improves our understanding of related electrochemical processes, which will contribute to the efficient production of Cu_2O thin films for diverse applications.

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