Light-Irradiated Electrochemical Direct Construction of Cu₂O/CuO Bilayers by Switching Cathodic/Anodic Polarization in Copper(II)—Tartrate Complex Aqueous Solution

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ABSTRACT: p-CuO with a band gap energy of 1.5 eV, p-Cu₂O with a band gap energy of 2.05 eV, and their bilayers were prepared by controlling the potential of anodic and cathodic polarization in a copper(II)−tartrate complex aqueous solution containing copper(II) sulfate hydrate and tartaric acid in the dark and under light irradiation. Electrochemical characteristics of the electrodeposition and the resultant CuO and Cu₂O layers were investigated with cyclic voltammetry, chronoamperometry, and Mott−Schottky plots, and the structural and optical characterizations were performed with X-ray diffraction, scanning electron microscopy, and optical absorption spectra measurements. The CuO layer prepared at 0.4−0.7 V was composed of aggregates of granular grains with the monoclinic lattice, and the Cu₂O layer composed of coarse grains with the cubic lattice was deposited at −0.4 to 0.6 V. The flat-band potentials were estimated to be 0.145 and −0.1 V (vs Ag/AgCl) for the CuO and Cu₂O layers, respectively. The 0.4 μm CuO/1.1 μm Cu₂O bilayers could be prepared by switching the electrodeposition potentials of 0.4 and −0.4 V, irrespective of the presence of light irradiation. The photoelectrodeposition under light irradiation enabled the preparation of continuous and dense 1.1 μm Cu₂O/0.4 μm CuO bilayer by controlling the potential, while electrodeposition in the dark led to sparse, isolated, and coarse Cu₂O grains being deposited. The mechanism for the photoelectrodeposition of the bilayers was discussed based on the energy band alignment at the heterointerface to the Cu−tartrate complex solution.

INTRODUCTION

Cupric oxide (CuO) and cuprous oxide (Cu₂O) are p-type semiconductors with band gap energies of 1.5 eV and 2.0 eV, and they both have been employed as photocathodes in photoelectrochemical water-splitting system for generating hydrogen gas and photovoltaic layer in oxide solar cells. The photoactive performance of the photocathode and photovoltaic layers closely relates to their band gap energy, and combining two or more p-type semiconductors with different band gap energies is an excellent strategy to enhance the performance, as demonstrated by the 38% efficiency InGaP/GaAs multijunction solar cell. A CuO/Cu₂O bilayer satisfying such a strategy was reported to act as a photocathode with superior performance compared to that of single CuO and Cu₂O layers.

The CuO and Cu₂O layers have been prepared by several techniques of thermal oxidation and solution chemical process. The solution chemical process offers several advantages over thermal oxidation and gas phase processes, such as saving energy due to low-temperature preparation and scalability for mass production, as demonstrated by the preparation of the precursors for Cu(In,Ga)Se₂ and Cu₂SnZnS₄ solar cells. Also, CuO/Cu₂O bilayers prepared by chemical processes, followed by heating, were also reported, but nanopores and defects introduced during heating showed harmful effects for the photoactive performance. The possibility of both CuO and Cu₂O layers being prepared by anodic and cathodic polarizations in an aqueous solution containing copper(II) sulfate and tartaric acid was reported by Poizot et al. Here, we report the electrochemical preparation of the CuO and Cu₂O layers by anodic and cathodic polarization in a modified copper(II)−tartrate complex aqueous solution and stacking of Cu₂O on CuO layers by electrodeposition was difficult because the electrons needed for the Cu₂O electrodeposition were the minority carriers in the p-CuO layer.

Here, we report the electrochemical preparation of the CuO and Cu₂O layers by anodic and cathodic polarization in a modified copper(II)−tartrate complex aqueous solution and stacking of Cu₂O on CuO layers by electrodeposition was difficult because the electrons needed for the Cu₂O electrodeposition were the minority carriers in the p-CuO layer.

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the direct, continuous constructions of CuO/Cu$_2$O and Cu$_2$O/CuO bilayers by irradiating light at photon energies higher than the underlying layer’s band gap energies during electrodepositions. Electrochemical characterization was carried out for the preparation of CuO, Cu$_2$O, and bilayers by cyclic voltammetry and chronoamperometry. Their structure and energy states including the band gap energies and flat-band potentials of the CuO and Cu$_2$O layers were investigated with X-ray diffraction, scanning electron microscopy (SEM) observation, optical absorption spectra measurement, and Mott–Schottky plots measurement. Furthermore, the mechanism of the photoelectrodeposition of CuO/Cu$_2$O bilayers was discussed based on the energy states of the CuO and Cu$_2$O layers.

## RESULTS AND DISCUSSION

### Electrochemical Preparation of CuO and Cu$_2$O Layers by Anodic and Cathodic Polarization

The change in the appearance of the aqueous solution containing a 0.3 mol L$^{-1}$ copper(II) sulfate and 0.3 mol L$^{-1}$ tartaric acid with pH value is shown in Figure S1. The pH value was adjusted using a NaOH aqueous solution. The solution color changed from the precipitation-free light blue at pH 1.1 to diluted light blue, cloudy dark blue, and clear dark violet over pH 11. The white precipitation was formed in the solution from pH 1.5 and then dissolved by raising the pH value, resulting in the precipitation was formed in the solution from pH 1.5 and then cloudy dark blue, and clear dark violet over pH 11. The white precipitation was formed in the solution from pH 1.5 and then dissolved by raising the pH value, resulting in the formation of this tartrate ligand requires at least 4 equiv NaOH to tartaric acid. The fact that the pH value $\sim$13 of the electrolyte containing 0.3 mol L$^{-1}$ tartaric acid and 1.5 mol L$^{-1}$ (5 equiv) NaOH is consistent with the formation of $\left[\text{Cu}_2(\text{H}_2\text{L})_2\right]^{4+}$. The expected structure of the $\left[\text{Cu}_2(\text{H}_2\text{L})_2\right]^{4+}$ complex and the calculated fraction of complex species$^{19}$ present depending on the solution pH are shown in Figure S2.

In the anodic polarization curve in Figure 1, the anodic current density increased from 0.27 V, and the black-colored CuO layer was deposited on the FTO substrate. The current densities were estimated to be 0.21, 0.65, 2.4, and 5.7 mA cm$^{-2}$ at 0.4, 0.5, 0.6, and 0.7 V, respectively. It has already been reported that the CuO electrodeposition by the anodic polarization from the Cu–NH$_3$ complex solution was induced by the oxygen gas generation reaction at the potential positive than that for the following reaction$^{14}$

$$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4 \text{e}^-$$

Since the potential of 0.27 V was close to 0.266 V for the oxygen gas generation reaction at pH 13, the formation of the CuO layer from the $\left[\text{Cu}_2(\text{H}_2\text{L})_2\right]^{4+}$ complex was induced by the oxygen gas generation reaction like the Cu–NH$_3$ complex solution.

When the potential was brought to the negative side, the cathodic current density gradually increased from $\sim$0.2 V and then rapidly increased from $\sim$0.6 V. The current densities were estimated to be $\sim$0.63, $\sim$0.65, $\sim$2.3, and $\sim$4.1 mA cm$^{-2}$ at $\sim$0.4, $\sim$0.5, $\sim$0.6, and $\sim$0.7 V, respectively. The red-colored Cu$_2$O layer was deposited from the $\left[\text{Cu}_2(\text{H}_2\text{L})_2\right]^{5+}$ complex at a potential more negative than $\sim$0.2 V, although the equilibrium potential could not be calculated due to absence of data on the thermodynamic property of the complex. Also, the potential of $\sim$0.5 V was close to that for the following reaction at pH 13

$$\text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Cu} + \text{H}_2\text{O}$$

Also, there was a possibility of the direct electrodeposition of metallic Cu from the $\left[\text{Cu}_2(\text{H}_2\text{L})_2\right]^{5+}$ complex.

Figure 2 shows the X-ray diffraction patterns of the CuO and Cu$_2$O layers prepared on FTO substrates by anodic polarizations at potentials from 0.4 to 0.7 V and cathodic polarizations at $\sim$0.4 to $\sim$0.7 V. Four peaks assigned as (002), (111), (111), and (200) planes with a characteristic monoclinic lattice$^{20}$ could be observed for the Cu$_2$O layer.
prepared at 0.4 V at 35.37, 35.59, 38.48, and 38.99°, respectively, in addition to those originating from SnO2 in the FTO substrate. The (002) peak disappeared and the (200) peak strengthened at potentials more positive than 0.5 V, indicating changes in the preferred orientation. The diffraction angles of (111) and (200) peaks were of almost constant values, irrespective of the potentials. The full width at half-maximum (FWHM) values of the CuO (111) plane were almost constant values of 0.32−0.34°, irrespective of the preparation potentials, which were smaller than 0.76° for a CuO layer prepared in a Cu−NH3 complex aqueous solution.15

The red-colored Cu2O layers prepared at −0.4 to −0.6 V showed X-ray peaks assigned as the (110), (111), and (200) planes of the characteristic cubic lattice at 29.6, 36.04, and 42.23°, and the intensity ratios were almost constant, irrespective of the potentials. Additionally, two additional peaks assigned as the (111) and (200) planes of metallic Cu were observed at −0.7 V. The deposition potential of −0.7 V was more negative than −0.5 V for the reduction reaction of Cu2O to Cu, and it was possible that trace metallic Cu was
incorporated in the Cu$_2$O layer at $-0.6$ V. The FWHM values of the Cu$_2$O (111) peak were almost constant values of 0.13°, irrespective of the preparation potentials.

Figure 3 shows the surface and cross-sectional structures of the CuO layers prepared at 0.4$-$0.7 V. The CuO layers were composed of aggregates of columnar grains with the size of approximately 0.48 μm, which were deposited over the entire surface of the FTO substrate without any defects, such as pores, on both the surface and cross-sectional structure. The grain morphology was significantly distinct from the fan-shaped grain of the CuO layer prepared on the FTO substrate in the Cu$-$NH$_3$ complex aqueous solution. The thicknesses of CuO layers were estimated to be 0.80, 0.58, 0.39, and 0.36 μm at 0.4, 0.5, 0.6, and 0.7 V, respectively. The change in the thicknesses was consistent with the decrease in the height of the CuO(111) peak shown in Figure 2, indicating the change in the current efficiency by the potential.

Figure 4 shows the surface and cross-sectional structures of Cu$_2$O layers prepared at $-0.4$ to $-0.7$ V. The cubic-shaped and isolated Cu$_2$O grains were deposited on the FTO substrate, with bare FTO substrate surface clearly observable between the Cu$_2$O grains. The size of the cubic Cu$_2$O grains decreased from 7.8 to 2.0 μm, and the grains’ density increased with change in potential from $-0.4$ to $-0.7$ V. At $-0.7$ V, 1.25 μm sized Cu$_2$O cubic grains were deposited over the entire FTO substrate, and additional cauliflower-shaped grains (shown by the arrow in Figure 4A(d)) were speculated to be metallic Cu as detected by the X-ray diffraction. A dense Cu$_2$O layer without any defect such as pores could be formed on the FTO substrates by cathodic polarization in a Cu-lactic acid aqueous solution. This shows that the solution formulation strongly affects the structure, including grain morphologies for both the CuO and Cu$_2$O layers.

Figure 5 shows the optical absorption spectra and the relationship between the absorption coefficient and photon energy for the CuO layers prepared at 0.4$-$0.7 V and Cu$_2$O layers prepared at $-0.4$ to $-0.7$ V. The absorption coefficients were estimated from the absorbance and layer thickness, and the grain height was used alternative to the thickness for the Cu$_2$O layers prepared at $-0.7$ V due to the vacancies between the Cu$_2$O grains. The Cu$_2$O layers possessed absorption edges at around 830 nm in wavelength, and the absorbance at 400 nm increased with increase in the CuO thickness. The absorption coefficient was almost constant at around $4 \times 10^4$ cm$^{-1}$, irrespective of the potential. The band gap energy ($E_g$) can be estimated by using the following relationship between $(\alpha h \nu)^n$ and photon energy ($h \nu$)

$$(\alpha h \nu)^n \propto (h \nu - E_g)$$

where $\alpha$, $h$, and $\nu$ are the absorption coefficient, Plank’s constant, and frequency of light, respectively, and $n$ is 2 or 1/2 for direct or indirect transition, respectively. The band gap energies were estimated to be 1.5 eV for all the CuO layers with the assumption of indirect transition, and this value
agreed with the one already reported. The CuO layers possessed absorption edges at around 610 nm, irrespective of the potentials, and the band gap energies were estimated to be 2.05 eV with the assumption of direct transition. The absorbance increased by decreasing vacancies between CuO grains when the potential was brought to the negative side from −0.4 to −0.7 V. The CuO layer prepared at −0.7 V showed a high absorbance at wavelengths longer than 610 nm due to the incorporation of opaque metallic Cu.

Figure 6 shows the flat-band potentials estimated from the Mott–Schottky plots (Figures S3 and S4) for CuO layers prepared at 0.4–0.7 V and Cu2O layers prepared at −0.4 to −0.7 V. The relationship between the space-change capacitance (C) and potential (E) in the Mott–Schottky plots is as follows

\[
\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 N_d \varepsilon_0 K T} \left( E - E_{fb} - \frac{K T}{e} \right)
\]

where \( \varepsilon, \varepsilon_0, N_d, K, T, \) and \( e \) are the permittivity of vacuum, dielectric constant of the semiconductor, carrier density, flat-band potential, Boltzmann constant, absolute temperature, and charge of electron, respectively. The flat-band potential is estimated by extrapolating the linear part to \( \frac{1}{C^2} = 0 \), and the carrier density corresponding to the acceptor density was estimated from the slope of the linear part. All of the CuO layers were p-type semiconductors, concluded from the negative slopes of the linear parts, irrespective of the potential. Also, the flat-band potentials (\( E_{fb} \)) were estimated to be approximate constant values of 0.149 ± 0.003 V (vs Ag/AgCl) for all CuO layers, irrespective of the potential. It has been reported for CuO layers prepared by electrodeposition in an aqueous solution containing a copper(II) sulfate and glycine, that the flat-band potential varied from 0.01 to 0.31 V (vs Ag/AgCl) depending on the solution pH, and the flat-band potential around 0.149 V was located within this variation. Also, a flat-band potential of 0.79 V (vs RHE) was reported for a CuO layer prepared by heating a Cu2O layer electro-deposited in a Cu–lactic acid aqueous solution, which is very close to 0.145 V (vs Ag/AgCl) obtained in this study. All of the CuO layers were identified as p-type semiconductors from the negative slopes of the linear parts for the Mott–Schottky plots, and the flat-band potentials (\( E_{fb} \)) were estimated to be −0.106, −0.09, and −0.080 V (vs Ag/AgCl) at the deposition potentials of −0.4, −0.5, and −0.6 V, respectively. A flat-band potential of 0.55 V (vs RHE) was reported for the CuO layer prepared by electrodeposition in the Cu–lactic acid aqueous solution and was close to those obtained at −0.4 to −0.6 V. A flat-band potential of −0.009 V for the Cu2O layer prepared at −0.7 V was different compared to the values obtained at −0.4 to −0.6 V due to the incorporation of metallic Cu. The flat-band potential (\( E_{fb} \)) closely relates to the Fermi level (\( E_F \)) of the CuO and Cu2O semiconductors, and the location of Fermi level (\( E_F \)) changed depending on the acceptor density (\( N_A \)) in the p-type semiconductor, as represented by the following equation

\[
E_F - VBM = \frac{K T \log \left( \frac{N_V}{N_A} \right)}{e}
\]

where VBM and \( N_V \) represent the valence band maximum and effective density of the state. The almost constant flat-band potentials reflected the almost constant acceptor densities for the CuO and Cu2O layers, except for the Cu-incorporated Cu2O layer prepared at −0.7 V. From the slope of the Mott–Schottky plots, the acceptor densities obtained for the CuO layers prepared at 0.4–0.7 V were in the order of 10^16 to 10^17 cm^-3 and for the Cu2O layers prepared at −0.4 to −0.6 V were in the order of 10^16 cm^-3. These values were close to those already reported for the CuO layers prepared by heating the Cu2O electrodeposits and for the Cu2O layers electrodeposited in the Cu(II)–lactic acid solution.

The effect of the insertion of the n-ZnO layer on the structure of CuO and Cu2O layers prepared at 0.4 and −0.4 V is shown in Figure S5. The insertion of the n-ZnO layer between the CuO layer and FTO substrate induced the change in CuO grain structure from isolated coarse grains (Figure 4) to a dense and continuous layer. The degree of the preferred orientation was estimated by calculating Harris’s texture coefficient, \( T_c \), by the following equation

\[
T_c = \frac{I_{h}(hkl) \sum_{i=1}^{n} I_{h}(hkl)}{I_{m}(hkl)}
\]

where \( I_{m}(hkl) \), \( I_{h}(hkl) \), and \( n \) are the relative intensity of the measured (hkl) peak, the relative intensity of the (hkl) peak of the standard sample, and the total number of peaks used for the calculation, respectively.

The \( T_c (111) \) for the CuO(111) plane was calculated by using the (110), (111), and (200) peaks and was estimated to be 0.7 and 1.4 for the Cu2O layers prepared on bare FTO and n-ZnO/FTO substrate. The n-ZnO layer possessed a (0001) preferred orientation from the X-ray diffraction pattern and maintains a lattice relationship of the (111) Cu2O//(0001) ZnO with a lattice mismatch of 7.1%. On the other hand, the orientation of the SnO2 layer in the FTO substrate was dispersed randomly. The n-ZnO layer and its orientation affected the grain structure and the preferred orientation of the resultant CuO layer. The insertion of the n-ZnO layer between the CuO layer and the FTO substrate showed no effects on the grain structure, thickness, and intensity ratio of the diffracted X-ray peaks of the CuO layer. There was a large lattice mismatch of over 15% for the (200) CuO//(0001) ZnO combination, and the lattice relationships between the monoclinic CuO and hexagonal ZnO lattices is a reason for no effects of the ZnO layer insertion on the electrochemical growth of the CuO layer. The potentials at 0.4 and −0.4 V were selected for the electrodeposition of CuO and Cu2O layers in bilayer constructions due to the small overpotential.

**Photoelectrodeposition of CuO/Cu2O Bilayers.** Figure 7 shows the chronoamperometry curves for the construction of CuO/Cu2O and CuO/Cu2O bilayers on the n-ZnO/FTO substrate by automatic switching of the potential in dark and under light irradiation from the SLG substrate side. The electric charge for the electrodeposition for both CuO and Cu2O layers was set at a constant absolute value of 1 C cm^-2. In the construction of the CuO/Cu2O bilayer in dark, the cathodic current density increased from zero to a maximum value of −1.86 mA cm^-2 when −0.4 V was applied for the CuO electrodeposition, and 662 s were needed for 1 C cm^-2 (Figure 7A(a)). The following current density rapidly changed to the anodic side when 0.4 V was applied for the CuO electrodeposition and reached a plateau region at around 0.637 mA cm^-2, which ended at 2,314 s in dark. The light irradiation induced an increase in the cathodic current density to −3.40
mA cm$^{-2}$, which decreased with the passage of the deposition time till 388 s for the Cu$_2$O electrodeposition, but no effect on the anodic current density was observed for the CuO electrodeposition (Figure 7A(b)). During the construction of the Cu$_2$O/CuO bilayer in the dark, the anodic current density for the CuO electrodeposition gradually increased to 0.871 mA cm$^{-2}$ at 2816 s, and the current density rapidly shifted to zero when $-0.4$ V was applied for the Cu$_2$O electrodeposition (Figure 7B(a)). The cathodic current density slowly increased to $-0.848$ mA cm$^{-2}$ at 5,676 s, showing that a deposition time of 2,860 s was needed for the Cu$_2$O electrodeposition of 1 C cm$^{-2}$. The light irradiation gave a slight increase in anodic current density to 1.23 mA cm$^{-2}$ and decreased slightly till 1,220 s (Figure 7B(b)). Applying $-0.4$ V for the Cu$_2$O electrodeposition induced a rapid change to the cathodic side with a maximum value of $-2.7$ mA cm$^{-2}$, and the deposition time for 1 C cm$^{-2}$ shortened to 531 s, compared to 2,860 s in dark. The light irradiation strongly affected the Cu$_2$O electrodeposition, but the effect was small for the CuO electrodeposition.

Figure 8 shows the surface and cross-sectional images of CuO/Cu$_2$O and Cu$_2$O/CuO bilayers prepared by switching the potential in the dark and under light irradiation. The CuO and Cu$_2$O layers in bilayers possessed characteristic monoclinic and cubic lattices with characteristic band gap energies of 1.50 and 2.05 eV, respectively, as shown in Figures S6 and S7. The CuO/Cu$_2$O bilayers prepared in the dark and under light irradiation were almost the same in terms of the grain structures and thicknesses for both the CuO and Cu$_2$O layers. The thickness of the CuO and Cu$_2$O layers were 0.4 and 1.0 μm, respectively, and the CuO layers composed of granular grains were deposited over the entire Cu$_2$O layer, irrespective of the light irradiation.

The light irradiation showed a drastic effect on the electrodeposition and structure of the Cu$_2$O layer on the CuO layer, although the structure and thickness of the CuO layer deposited on the n-ZnO/FTO substrate were almost the same in the dark and under light irradiation. The isolated Cu$_2$O grains approximately 2 μm in size were deposited sparsely on the CuO layer, and the underlying CuO surface could be observed between the Cu$_2$O grains when deposited in the dark. The light irradiation contributes to the formation of continuous and dense Cu$_2$O layer composed of the 2 μm size coarse grains without any pores.

Figure 9 shows the schematic illustration of the mechanism for photoelectrodeposition of the CuO layer on the Cu$_2$O layer and vice versa. The flat-band potentials were estimated to be 0.145 and $-0.106$ V referenced to Ag/AgCl electrode for the CuO layer prepared at 0.4 V and Cu$_2$O layer prepared at $-0.4$ V. In the anodic deposition of the CuO layer on the Cu$_2$O layer, the holes ($h^+$), that are the majority carriers, are swept toward the Cu(II)–tartrate complex solution by the electric field formed at the heterointerface at an applied potential of 0.4 V. Also, the ejected holes cause the anodic deposition (AD) of a layer from the alkaline Cu(II)–tartaric acid solution (pH ~13), which is mainly composed of $[\text{Cu}_2(\text{H}_2\text{L})_2]^{4+}$, by the plausible mechanism as follows:

$$(\text{AD} - \text{i})\text{H}_2\text{O} + 4h^+ \rightarrow \text{O}_2 + 4\text{H}^+$$
The cathodic potential applied to the FTO substrate decomposes H2O to generate H+, decreasing the local pH on the substrate surface (AD-i). The [Cu2(H2L)2]+ complex is partially protonated to give [Cu2(H−L)2]2−, which is unstable in the alkaline region,22 causing the precipitation of Cu(OH)2 on the substrate (AD-ii, iii). Subsequently, CuO crystals grow through the dehydration of Cu(OH)2 (AD-iv). A similar mechanism has been proposed for the anodic deposition of Ag2O from an alkaline Cu(II) tartrate complex solution,33 including the bilayers and further multilayers.

The p-CuO layers with the 1.5 eV band gap energy and monoclinic lattice, p-Cu2O layers with the 2.05 eV band gap energy and cubic lattice, and bilayers consisting of both have been prepared by controlling the potential in an aqueous solution containing copper(II) sulfate hydrate and tartaric acid in the dark and under light irradiation. The CuO layers were composed of granular grains on the FTO substrate with and without the n-ZnO layer, irrespective of the light irradiation. The isolated and coarse Cu2O grains were deposited sparsely on the FTO substrate, but the insertion of the n-ZnO layer induced the change to a continuous and dense layer, irrespective of the light irradiation. The flat-band potential was estimated to be at almost constant values of 0.149 V versus Ag/AgCl for CuO layers prepared at 0.4 to 0.7 V and approximately −0.10 V for Cu2O layers prepared at −0.4 to −0.6 V. The 0.4 μm CuO/1.1 μm Cu2O bilayers with characteristic grain structures could be prepared by cathodic polarization at −0.4 V, followed by an anodic polarization at 0.4 V, irrespective of the light irradiation. The electro-deposition of the Cu2O layer on the CuO layer was strongly affected by the light irradiation and continuous and defect-free 1.1 μm Cu2O/0.4 μm CuO bilayers could be prepared by anodic polarization at 0.4 V, followed by cathodic polarization at −0.4 V under the light irradiation. The mechanism for the photoelectrodeposition of CuO/Cu2O and Cu2O/CuO bilayers was discussed based on the energy band alignments drawn based on the flat-band potentials and applied potentials for the electodeposition. The results demonstrated here reveals the ability to construct nanostructured oxide layers including the bilayers and further multilayers.

**CONCLUSIONS**

Aqueous solution containing 0.3 mol L−1 copper(II) sulfate hydrate, 0.3 mol L−1 tartaric acid, and 1.5 mol L−1 sodium hydroxide was used for the electrodeposition of CuO, Cu2O, and bilayers, respectively, with a solution pH of 13.0. The electrodepositions were performed for CuO layers at potentials

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**EXPERIMENTAL SECTION**

An aqueous solution containing 0.3 mol L−1 copper(II) sulfate hydrate, 0.3 mol L−1 tartaric acid, and 1.5 mol L−1 sodium hydroxide was used for the electrodeposition of CuO, Cu2O, and bilayers, respectively, with a solution pH of 13.0. The electrodepositions were performed for CuO layers at potentials

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**Figure 9.** Schematic illustrations for the photoelectrochemical deposition of CuO on Cu2O layer (a) and Cu2O on CuO layer (b).
of 0.4, 0.5, 0.6, and 0.7 V and for Cu₂O layers at −0.4, −0.5, −0.6, and −0.7 V, respectively, referenced to Ag/AgCl electrode for an electric charge of 1 C cm⁻² with a Pt counter electrode using a polarization system (Hokuto Denko, HSV-110) connected with a Coulomb meter (Hokuto Denko, HF301), and the solution temperature was kept at 323 K. The CuO/Cu₂O and Cu₂O/CuO bilayers were fabricated by automatically switching the potential with the polarization system in dark and under light irradiation. The light was irradiated from the side of the glass substrate using a high-pressure mercury lamp (USHIO, OPTICAL-MODULEX, 500 W) without any optical filter. The ZnO layer was prepared by electrodeposition on the FTO substrate in an aqueous solution containing 80 mmol L⁻¹ zinc nitrate hydrate at −0.8 V referenced to an Ag/AgCl electrode and 335 K for an electric charge of 0.5 C cm⁻² using a potentiostat (Hokuto Denko, HAL 3000) connected with a Coulomb meter (Hokuto Denko, HF 301). The solution was prepared using reagent grade chemicals and distilled water purified with Milli Pore Milli-Q Advantage. F:SnO₂/soda-lime glass (FTO, AGC Fabritech, Co. Ltd., 10 Ω cm⁻¹) was used as the substrate. Prior to the electrodeposition, the FTO substrates were degreased by anodic polarizations in a 1 mol L⁻¹ sodium hydroxide aqueous solution.

Cyclic voltammetry and chronoamperometry measurements were performed using the polarization system (Hokuto Denko, HSV-110). The X-ray diffraction patterns were recorded by a θ/2θ scanning technique with monochromated Cu Kα radiation operated at 40 kV and 200 mA using a Rigaku RINT2500. The optical absorption spectra were measured by recording the absorbance using a UV–vis–NIR spectrophotometer (Hitachi, U4100) with an integrated sphere, and the X-ray diffraction measurements were performed using a Rigaku XRD-3000. The CuO/Cu₂O and Cu₂O/CuO bilayers were fabricated by automatically switching the potential with the polarization system in dark and under light irradiation. The light was irradiated from the side of the glass substrate using a high-pressure mercury lamp (USHIO, OPTICAL-MODULEX, 500 W) without any optical filter. The ZnO layer was prepared by electrodeposition on the FTO substrate in an aqueous solution containing 80 mmol L⁻¹ zinc nitrate hydrate at −0.8 V referenced to an Ag/AgCl electrode and 335 K for an electric charge of 0.5 C cm⁻² using a potentiostat (Hokuto Denko, HAL 3000) connected with a Coulomb meter (Hokuto Denko, HF 301). The solution was prepared using reagent grade chemicals and distilled water purified with Milli Pore Milli-Q Advantage. F:SnO₂/soda-lime glass (FTO, AGC Fabritech, Co. Ltd., 10 Ω cm⁻¹) was used as the substrate. Prior to the electrodeposition, the FTO substrates were degreased by anodic polarizations in a 1 mol L⁻¹ sodium hydroxide aqueous solution.

Cyclic voltammetry and chronoamperometry measurements were performed using the polarization system (Hokuto Denko, HSV-110). The X-ray diffraction patterns were recorded by a θ/2θ scanning technique with monochromated Cu Kα radiation operated at 40 kV and 200 mA using a Rigaku RINT2500. The optical absorption spectra were measured by recording the absorbance using a UV–vis–NIR spectrophotometer (Hitachi, U4100) with an integrated sphere, and the bare substrate was used as the reference. Electron microscopy observations were carried out at an accelerating voltage of 5 kV using field-emission scanning electron microscopy (SEM, Hitachi, SU8000). An electrochemical impedance measurement was performed in a 0.1 mol L⁻¹ sodium sulfate aqueous solution at pH 6.0 at room temperature by using VersaSTAT 3-100 (Princeton Applied Research), and Mott–Schottky plots were drawn by using a VersaStudio software (Princeton Applied Research).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03308.

- Solution appearance; complex species; Mott–Schottky plots; X-ray diffraction patterns; absorption spectra for bilayers (PDF)

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### Author Contributions

M.I. conceived the project, designed the experiments, and analyzed data. T.K., P.L.K., and T.S. carried out the material preparation and most of characterizations. All authors discussed the results and commented on the manuscript.

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Notes

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