

Electrochemical Oxidation of Glucose using Copper Hydroxide Nanosheets

M. Kurashina^a, F. Suzuka^a, and M. Yasuzawa^a

^a Department of Applied Chemistry, Graduate School of Science and Technology, Tokushima University, Tokushima-shi, Tokushima 770-8506, Japan

In this study, we synthesized copper hydroxide nanosheet and investigated electrochemical oxidation of glucose using the copper hydroxide nanosheets. The precursor of the nanosheet was a layered copper hydroxide synthesized by the ion exchange of dodecylbenzene sulfonate with acetate in $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$. Delamination of the layered copper hydroxide prepared the nanosheet by dispersion in 1-butanol. Atomic force microscopy images of the nanosheets showed lateral dimensions of ca. 2 μm with a height of ca. 4.5 nm. Cyclic voltammogram of the nanosheet coated electrode showed oxidation current peak depend on the concentration of glucose at around +0.6 V vs. Ag/AgCl. Amperometry was measured at +0.6V vs. Ag/AgCl with successive addition of glucose solution. Glucose concentration and catalytic current were almost proportional. When the linear range is 0.1 to 4.9 mM, the sensitivity was 1.16 mA $\text{mM}^{-1}\text{cm}^{-2}$ from the slope.

Introduction

Non-enzymatic electrocatalysts have recently received much attention as a glucose sensor (1) and biofuel cell (2). These catalysts contain transition metals such as Pt, Au, Ni, and Cu. The glucose adsorbs onto the surface of the catalytic electrode and is oxidized by hydroxyl radicals. Smaller structured materials make the surface area larger, thus nanostructured electrode is expected to show efficient oxidation of glucose. As a nanomaterial, nanosheets have recently received much attention as a new material with an ultimate two-dimensional anisotropy. Inorganic nanosheets have been prepared by delamination of layered materials, such as titania, manganate, niobate, layered perovskite, transition metal chalcogenides, and layered double hydroxide (3). We synthesized copper hydroxide in which dodecylbenzene sulfonate intercalated and delamination of these compounds to monolayer nanosheets (4). Copper oxide and hydroxide are viable candidates for the non-enzymatic electrochemical glucose sensor. Thus copper hydroxide nanosheets are expected to make novel non-enzymatic electrochemical glucose sensor. In this study, we synthesized copper hydroxide nanosheet and investigated its electrochemical oxidation of glucose.

Experiments

The precursor of the nanosheet was a layered copper hydroxide synthesized by the ion exchange of dodecylbenzene sulfonate with acetate in $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$. The $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$ was synthesized by hydrolysis of $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ solution (0.1 M) by heating at 65 °C for several days until crystalline product formed (5). The

$\text{Cu}(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$ (0.042 g) was added to the solution of NaDBS (DBS^- = dodecylbenzene sulfonate, 26.6 mM, 40 mL) and shaken at 30 °C for 18 h. The precipitate was separated by centrifugation and washed with water and air dried. The yielded product (0.053 g) is named as Cu-DBS.

Delamination of Cu-DBS prepared the nanosheet by dispersion in 1-butanol. The Cu-DBS (0.03 g) in 1-butanol (45 mL) was shaken and let stand for 2-4 weeks and resulted in the dispersion. The supernatant of the dispersion was used to further measurements.

The 15 g of the dispersion of the copper hydroxide nanosheet was concentrated by an evaporator and dried after dropped on the ϕ 3 mm glassy carbon (GC) electrode. This GC electrode was used as a working electrode. Electrochemical measurements of this working electrode were carried out in a standard one-compartment cell equipped with an additional bare GC working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode in 0.1 M NaOH solution.

Results and Discussions

Atomic Force Microscopy Images of the Copper Hydroxide Nanosheets

The morphology and size of nanosheets in the dispersion were examined by atomic force microscopy (AFM), which revealed a nanosheet structure. The examined samples were prepared by deposition of a droplet of the dispersion on a silicon wafer. Intermittent contact mode AFM images (Figure 1) showed two-dimensional ultrathin sheets with the lateral dimensions of ca. 2 μm . Some aggregates were occasionally observed. The height profile reveals that the sheets have a reasonably flat terrace with a thickness of 4.33–6.30 nm with 320–460 aspect ratio and some sheets are stacked step by step with keeping the height. If DBS^- ions place perpendicular to the hydroxide layer, the minimum thickness of the sheets should be ca. 5 nm because DBS^- ions (22–25 Å) coordinate the hydroxide layer both on surfaces of the copper hydroxide sheet. Therefore DBS chains would align closely with the hydroxide layers at an angle of ca. 40 °. These copper hydroxide nanosheets are thin enough to be considered as a monolayer.

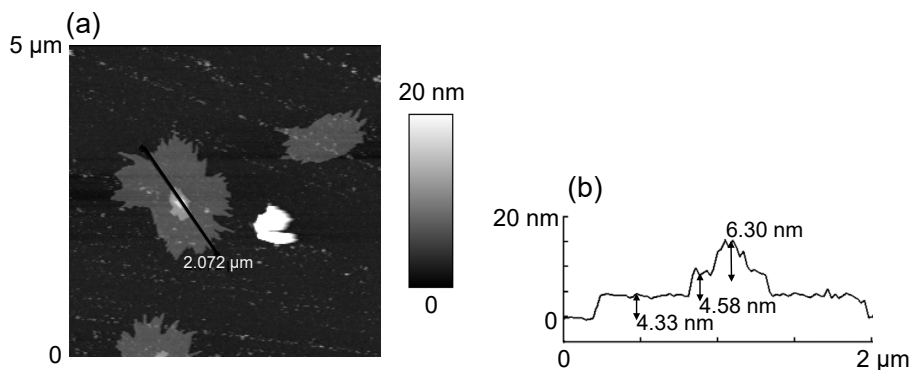


Figure 1. AFM images of the copper hydroxide nanosheets deposited on a silicon wafer (a) and the cross-sectional view (b).

Electrochemical Properties of the Copper Hydroxide Nanosheets

Cyclic voltammetry (CV) was measured at 20 mV/s scan rate after addition of glucose solution to 0-2 mmol/l concentration (Figure 2). The CV of the nanosheet coated electrode showed an oxidation current peak at around +0.6 V vs. Ag/AgCl, and this peak current increased as the concentration of glucose increased. This peak was not detected with only the GC electrode thus current peak was caused by the oxidation of glucose.

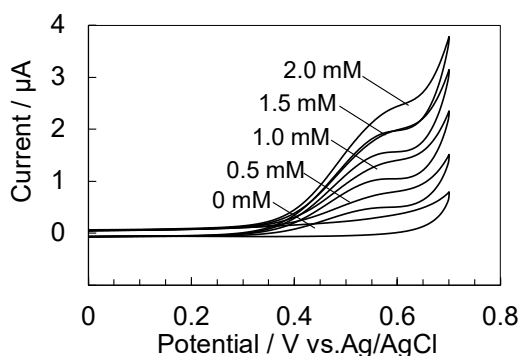


Figure 2. CV of the copper hydroxide nanosheets with a concentration of glucose.

Amperometry was measured at +0.6V vs. Ag/AgCl with successive addition of glucose solution (Figure 3). The concentration of glucose increased to 0.1 to 27.8 mM, the current of the nanosheet coated electrode increased in a stepwise when glucose solution was added. The current was not detected with only the GC electrode. Glucose concentration and catalytic current were almost proportional. When the linear range is 0.1 to 4.9 mM, the sensitivity was $1.16 \text{ mA mM}^{-1}\text{cm}^{-2}$ from the slope. This value is comparable to the other glucose electrolytic oxidation electrodes using copper (6).

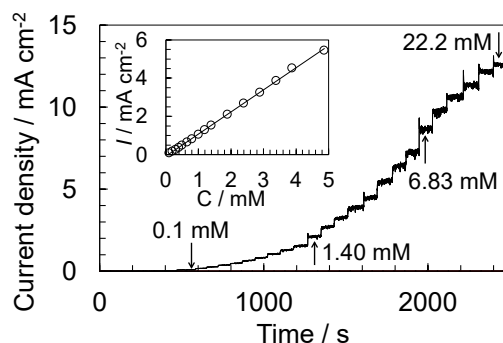


Figure 3. Amperometric response of the copper hydroxide nanosheets with the successive addition of glucose. The inset shows the corresponding calibration curve.

Conclusions

We synthesized copper hydroxide nanosheet and investigated electrochemical oxidation of glucose using the copper hydroxide nanosheets. The precursor of the nanosheet was a layered copper hydroxide synthesized by the ion exchange of dodecylbenzene sulfonate with acetate in $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$. Delamination of the layered copper hydroxide prepared the nanosheet by dispersion in 1-butanol. Atomic force microscopy images of the nanosheets showed lateral dimensions of ca. 2 μm with a height of ca. 4.5 nm. Cyclic

voltammogram of the nanosheet coated electrode showed oxidation current peak depend on the concentration of glucose at around +0.6 V vs. Ag/AgCl. Amperometry was measured at +0.6V vs. Ag/AgCl with successive addition of glucose solution. Glucose concentration and catalytic current were almost proportional. When the linear range is 0.1 to 4.9 mM, the sensitivity was 1.16 mA mM⁻¹cm⁻² from the slope. It is expected that this copper hydroxide nanosheet is applied to be a new glucose sensor electrode and a biofuel cell.

References

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