

## SYNTHESES AND PROPERTIES OF COPPER HYDROXIDE NANOSHEETS AND CONTROLLED DEPOSITION

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In this study, we synthesized copper hydroxide nanosheet and investigated its electrochemical property and how to deposit it with a uniform amount. 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 nanosheet was prepared by delamination of the layered copper hydroxide by dispersion in 1-butanol. Atomic force microscopy images of the nanosheets showed lateral dimensions of ca. 2  $\mu\text{m}$  with the height of ca. 4.5 nm. Cyclic voltammogram of the nanosheet in basic solution showed two cathodic peaks and two anodic peaks similar to copper oxide electrode. To deposit the nanosheet, a quartz glass slide was dipped in the dispersion of the nanosheet in 1-butanol and dried after washing. This procedure was repeated and the ultraviolet and visible light absorption spectrum of the slide was measured. The absorbance of the slide increased in direct proportion to the number of times of the dip-and-dry procedure. Thus we confirmed that controlled amount of nanosheet was deposited on the quartz glass.

*Keywords:* Nanosheet; copper hydroxide; electrochemical property; deposition

### 1. Introduction

Nanosheets have recently received much attention as a new material. Nanosheet has an ultimate two-dimensional anisotropy and manifests unique physical properties arising from size effects. Inorganic nanosheets have been prepared by delamination of layered materials, such as titania, manganate, niobate, layered perovskite, transition metal chalcogenides, and layered double hydroxide.<sup>1</sup> These nanosheets show interesting properties and potential for use such as sensors, non-linear optical materials, catalysis, and electrochemical materials.<sup>2</sup> We have already reported syntheses of cobalt and nickel hydroxide in which dodecylbenzene sulfonate intercalated and delamination of these compounds to monolayer nanosheets.<sup>3</sup> On the other hand, copper oxide has been attracted attention as a viable candidate for non-enzymatic electrochemical glucose sensor.<sup>4</sup> Thus syntheses of copper contained nanosheets and fabrication of them are expected to make novel non-enzymatic electrochemical glucose sensor.

In this study, we synthesized copper hydroxide nanosheet and investigated its electrochemical property and how to deposit it with a uniform amount.

## 2. Experiments

The  $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$  was synthesized in two ways by reference to the literature. One way<sup>5</sup> is the slow addition of NaOH solution (0.1 M) using a syringe driver to  $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$  solution (0.1 M) with vigorously stirred at 50 °C. The other way<sup>6</sup> is 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. 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<sup>-</sup> = 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 3 times and air dried. The yielded product (0.053 g) is named as Cu-DBS.

To make dispersion, the Cu-DBS (0.04 g) in 1-butanol (40 mL) was shaken and let stand for over 1 week. The supernatant of the dispersion was used to further measurements.

## 3. Results and Discussions

### 3.1. Syntheses and Characterizations of Layered Copper hydroxides

We synthesized Cu-DBS by the ion-exchange of acetate in  $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$  with DBS<sup>-</sup>. X-ray diffractions (XRD) patterns of  $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$  and Cu-DBS were measured to determine the crystal structures. From the literature<sup>6</sup>,  $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$  is crystallized in monoclinic system and its layers consist of two-dimensional distorted triangle arrays of Cu(II) ions axially elongated octahedral coordinated by six hydroxo or acetate ligands. The hydroxide layers are stacked along the axis perpendicular to  $a_0$  and  $b_0$  and form the layered structure. The interlayer distance of the layered  $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$  was calculated from the largest peak at  $2\theta = 9.40^\circ$  as 9.41 Å. XRD patterns of Cu-DBS showed peaks at  $2\theta = 2.72, 5.52, 8.32, 11.12, 13.92^\circ$ . These XRD patterns are assigned to 00 $l$  diffraction and characteristic of layered materials. The interlayer distance of the Cu-DBS was calculated from the largest peak at  $2\theta = 2.72^\circ$  as 32.48 Å. The difference of the interlayer distance between  $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$  and Cu-DBS is due to the different size of the intercalated ions, acetate (3–4 Å) and DBS<sup>-</sup> ion (22–25 Å).

### 3.2. Atomic Force Microscopy Images of the Copper Hydroxide Nanosheets

The morphology and size of nanosheets in the dispersion of were examined by atomic force microscopy (AFM), which revealed nanosheet structure. The examined samples were prepared by deposition of a droplet of the colloidal solution on a silicon wafer. Intermittent contact mode AFM images (Fig. 1 left) 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 fairly 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  $\text{DBS}^-$  ions place perpendicular to the hydroxide layer, the minimum thickness of the sheets should be ca. 5 nm because  $\text{DBS}^-$  ions (22–25 Å) coordinate the hydroxide layer both on surfaces of the copper hydroxide sheet. Therefore DBS chains would align closely to the hydroxide layers at an angle of ca.  $40^\circ$  in a similar manner to the result of cobalt and nickel hydroxide nanosheets.<sup>3</sup> These copper hydroxide nanosheets are thin enough to be considered as a monolayer.

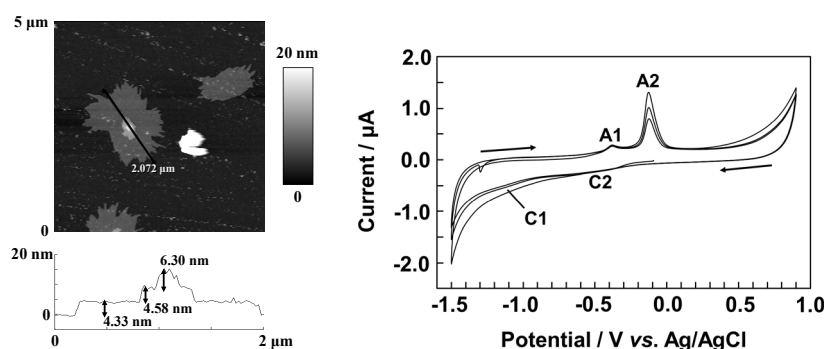


Fig. 1. AFM images of the copper hydroxide nanosheets deposited on a silicon wafer (upper left) and the cross-sectional view (bottom left). CV of the copper hydroxide nanosheets on a glassy carbon disk (right).

### 3.3. Electrochemical properties of the Copper Hydroxide Nanosheets

The 2 mL of dispersion of the copper hydroxide nanosheet was concentrated by an evaporator and dried after dropped on the  $\phi$  3 mm glassy carbon electrode. Cyclic voltammetry (CV) of this working electrode was carried out under a nitrogen atmosphere in a standard one-compartment cell equipped with a platinum-wire counter electrode and an Ag/AgCl reference electrode in 0.1 M NaOH solution at a scan rate of 20 mV/sec. Cyclic voltammogram (Fig. 1 right) of the copper hydroxide nanosheet indicated two cathodic peaks at C2 (−0.52 V) and C1 (−1.16 V) and followed two anodic peaks at A1 (−0.37 V) and A2 (−0.13 V). These behavior are very similar to the cyclic voltammogram of copper oxide electrode<sup>7</sup> thus C1 and A1 are assigned to redox of Cu(I) (such as  $\text{Cu}_2\text{O}$ ) and Cu(0), and C2 and A2 are assigned to redox of Cu(II) (such as  $\text{CuO}$  and  $\text{Cu}(\text{OH})_2$ ) and Cu(I).

### 3.4. Controlled Deposition of the Copper Hydroxide Nanosheets.

To assemble these nanosheets, a quartz glass slide was dipped in the dispersion of each hydroxide nanosheet in 1-butanol and dried after washing. This procedure was repeated several times and the ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectrum of the slide was measured. It is the 1 cycle of dip-and-dry procedure, and we repeated this procedure and measured changes of UV-Vis-NIR absorption spectra. In Fig. 2 left, absorption change from a quartz glass slide before used (named as 0 cycles) were shown in the case of 5 minutes immersion time. Absorbances of these slides were increased as the

dip-and-dry procedure was repeated. The absorbance changes were ranged from 200-1900 nm thus they caused by the increase of turbidity of the quartz glass slide. The absorption change at 200 nm depending on total immersion time and numbers of measurement times were plotted in Fig. 2 right in the case of 5, 30, and 60 minutes immersion time per 1 cycle. The absorbance increased in nearly direct proportion to times of the dip-and-dry procedure. Especially, it aligned along the same line depending on the numbers of measurement times. This result means the amount of deposition of the copper hydroxide nanosheet can be controlled by the cycle numbers of the dip-and-dry procedure.

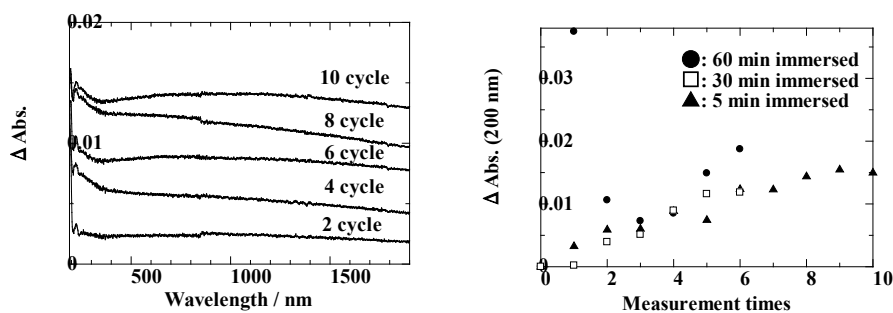


Fig. 2. UV-Vis-NIR spectra of quartz glasses slide after 0-10 cycles immersed in the copper hydroxide nanosheets dispersion in the case of 5 minutes immersion time (left). Absorbance change at 200 nm after immersed in the copper hydroxide nanosheets dispersion depending on numbers of measurement times (right).

#### 4. Conclusions

We synthesized the copper hydroxides nanosheets by means of dispersion of layered compounds. AFM images of the nanosheets showed lateral dimensions of ca. 2  $\mu$ m with the height of ca. 4.5 nm. Cyclic voltammogram of the nanosheet showed redox similar to copper oxide electrode. The deposition of the nanosheet can be controlled by the cycle numbers of the dip-and-dry procedure. It is expected that functions of the nanosheets will be developed by combining electrochemical properties with controlled deposition.

#### References

1. K. Kuroda and T. Sasaki, *Science and Applications of Inorganic Nanosheets* (CMC Publishing, Tokyo, 2005).
2. K. Ariga, Q. Xu, T. Kimura, Y. Kubota and Y. Yamauchi, *Nanospace Materials Handbook* (NTS Inc., Tokyo, 2016).
3. M. Kurashina, A. Eguchi, E. Kanezaki, T. Shiga and H. Oshio, *Int. J. Mod. Phys. B* **24**(15-16), 2291 (2010).
4. G. Wang, X. He, L. Wang, A. Gu, Y. Huang, B. Fang, B. Geng and X. Zhang, *Microchimica Acta* **180**(3), 161 (2013).
5. K.-I. Sotowa, T. Togawa, Y. Shimizu, M. Kurashina, T. Horikawa and J. R. Alcantara Avila, *Appl. Mech. Mater.* **625**, 201 (2014).
6. S. Švarcová, M. Klementová, P. Bezdička, W. Łasocha, M. Dušek and D. Hradil, *Cryst. Res. Technol.* **46**(10), 1051 (2011).
7. H. Y. H. Chan, C. G. Takoudis and M. J. Weaver, *J. Phys. Chem. B* **103**(2), 357 (1999).