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4 **Preparation of Plate-like Copper Nitride Nanoparticles from a Fatty Acid Copper(II) Salt and**
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6 **Detailed Observations by High Resolution Transmission Electron Microscopy and High-angle**
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8 **Annular Dark-field Scanning Transmission Electron Microscopy**
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11 Takashi Nakamura,* Norihito Hiyoshi, Hiromichi Hayashi, and Takeo Ebina
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13 Research Center for Compact Chemical System, National Institute of Advanced Industrial Science and
14
15 Technology (AIST), Nigatake 4-2-1, Miyagino-ku, Sendai, Miyagi 983-8551, Japan
16
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18 E-mail: nakamura-mw@aist.go.jp
19
20

21 Tel: +81-29-861-2272
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24 **Abstract:** We recently developed a new method to prepare copper nitride nanoparticles without the use of
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26 high pressure or high temperature. In this study, we used the method to prepare plate-like copper nitride
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28 nanoparticles from copper(II) decanoate as a precursor. XRD and HR-TEM analyses revealed that the
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30 (100) plane grew selectively under the reaction conditions. HAADF-STEM clearly showed atomic
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32 columns of copper at different sites in the copper nitride crystal.
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36 **Keywords:** copper nitride, nanoparticles, HAADF-STEM, printed electronics, wiring material
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39 **1. Introduction**
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41 Copper nitride (compositional formula, Cu_3N) was first prepared by Juza and Hahn in 1938 for
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43 characterization of its crystal structure as a cubic anti- ReO_3 structure (space group, $Pm-3m$),[1] and since
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45 then, it has been the subject of extensive research, both basic and applied. It is a candidate for use as a
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47 light recording medium,[2] a resistive random access memory component,[3] a cathode catalyst,[4] and a
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49 wiring material for printed electronics.[5, 6] We believe that copper nitride nanoparticles are particularly
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51 promising as a wiring material because they decompose to copper and nitrogen when heated.
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54 Copper nitride nanoparticles have been synthesized by various methods, including ammonolysis,[7]
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56 solvothermal synthesis,[8] and amine solvent methods.[4, 9] A process using octadecylamine as a solvent
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is especially suitable for preparing finely dispersed nanoparticles with cubic crystal structure.[4, 9]

Our group recently developed a novel method, referred to as alcohol-reducing nitridation, for the preparation of copper nitride nanoparticles.[5] The method is easy and safe because it can be carried out at atmospheric pressure and at relatively low temperature (<200 °C). The method can be used to prepare nanoparticles with cubic crystal structure.

The chemical properties of nanoparticles show crystal plane dependence and shape dependence; for example, molecular chemisorption[10] and catalytic activity[11] have been shown to vary widely with morphology. Copper nitride nanoparticles have not been studied as extensively as other copper-based nanoparticles, such as copper and copper(II) oxide nanoparticles, and therefore investigation of the effects of particle shape and crystal structure on copper nitride properties is necessary to expand its applications.

Here we report the preparation of plate-like copper nitride nanoparticles from a fatty acid copper(II) salt precursor. We measured the X-ray diffraction (XRD) patterns of the nanoparticles and estimated their anisotropy ratio. In addition, we used high-resolution transmission electron microscopy (HR-TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) to observe their crystal structure at the atomic level.

2. Experimental

Copper(II) decanoate (CuC10) was prepared by a previously reported procedure with modifications.[12, 13] Specifically, sodium octanoate was changed to sodium decanoate. To prepare copper nitride, a dispersion of CuC10 (2 mmol) in 1-nonanol (400 mL) was bubbled with ammonia (100 mL/min) and heated at 190 °C for 40 min (ramp time, 10 min; hold time, 30 min) in a μ Reactor Ex microwave heater (2.45 GHz, Shikoku Instrumentation) equipped with a fiber-optic thermometer (AMOTH FL-2000, Anritsu Meter Co.). The temperature of the solution was controlled by automatically changing the microwave power. The opaque black liquid that was obtained from the reaction was supercentrifuged (30,000g for 60 min) to afford a black powder, which was washed three times with *n*-hexane. For comparison, copper nitride nanoparticles were also prepared from copper acetate (CuC2) by

means of the same procedure.[13]

The crystal structures of the obtained powders were characterized by XRD analysis with Cu K α radiation at 40 kV and 30 mA at $2\theta = 20\text{--}90^\circ$ (recording interval, 0.02°) with a SmartLab diffractometer (Rigaku) and an Al sample holder. TEM images of the powder were obtained with a TECNAI G20 instrument (FEI) as described in a previous publication.[5] To record HR-TEM and HAADF-STEM images, we used a JEM-ARM200F microscope (JEOL) equipped with a cold-field emission gun and an aberration corrector for STEM operated at an acceleration voltage of 200 kV. The TEM images were recorded with a 2048×2048 pixel CCD camera (UltraScan 1000XP, Gatan). For the HAADF-STEM image, the annular detector was set to collect electrons scattered at angles from 68 to 175 mrad.

3. Results and discussion

The XRD patterns of the powders prepared from CuC10 and CuC2 (Figure 1) were analyzed to estimate peak tops and full widths at half-maximum (FWHMs) of the peaks by curve fitting with the pseudo-Voigt function. The XRD pattern of the powder prepared from CuC10 showed peaks at 23.38° , 33.25° , 41.02° , 47.79° , and 53.79° , which were attributed to the (100), (110), (111), (200), and (210) planes of copper nitride (PDF2 no. 01-073-6209), respectively (Estimated d -spacings are listed in the Supplementary Information). The XRD pattern of the powder prepared from CuC2 showed peaks at 23.38° , 33.29° , 41.05° , 47.77° , and 53.85° , again attributed to the (100), (110), (111), (200), and (210) planes of copper nitride, respectively. Both samples contained only one crystalline phase of copper nitride, and there were no byproduct phases such as metallic copper, copper(I) oxide, or copper(II) oxide. Interestingly, the (110) and (111) peaks of the copper nitride prepared from CuC10 were broader than the corresponding peaks of the copper nitride prepared from CuC2. Peak broadening can indicate a decrease in crystallite average size, an increase in crystallite strain, and an increase in the distribution of crystallite sizes. In this case, we assumed that the peak broadening was due to a change in only crystallite size without influence of crystallite strain and the distribution of particle sizes (Estimation of crystal strain of copper nitride nanoparticles are described in the Supplementary Information).[13] The crystallite sizes for

the (100), (110), and (111) planes were estimated by means of the Scherrer equation using the FWHMs and a value of 0.94 for the Scherrer constant; then the ratios of the crystallite sizes of the (110) and (111) planes to the crystallite size of the (100) plane were calculated as estimates of the anisotropy ratio of the copper nitride (Table 1). Here anisotropy ratio reflects crystallite average sizes of the nanoparticles obtained from each reagent.

When CuC10 was used as the precursor, the (110)/(100) and (111)/(100) ratios were larger than the corresponding ratios for the sample prepared from CuC2. This result indicates that the (100) plane of copper nitride grew preferentially when the fatty acid copper(II) salt was used as the precursor.

The morphology of the copper nitride nanoparticles was observed by TEM. The copper nitride prepared from CuC10 contained plate-like and rod-like particles (Figure 2a). By means of HR-TEM observations and XRD analysis, it was concluded that the rod-like particles are the plate-like particles viewed edge-on (the reasons are described later). The rod-like particles were approximately 20 and 5 nm in the directions of the long and short axes, respectively. The nanoparticles prepared from CuC2 were secondary particles with diameters of approximately 100 nm and consisted of primary particles having dimensions of approximately 30 nm on a side (Figure 2b). The contrast of the primary particles was homogeneous and darker than that of the particles prepared from CuC10.

The XRD and TEM results indicated that anisotropic copper nitride nanoparticles were obtained and the sizes of primary particles were minimized by using the fatty acid copper(II) salt as a precursor.

To confirm the direction of crystal growth, we obtained HR-TEM and HAADF-STEM images of the plate-like copper nitride nanoparticles, which are prepared from CuC10, viewed from horizontal (Figure 3a) and vertical direction (Figure 3b). HR-TEM image of the nanoparticles viewed from horizontal direction also indicated that they were approximately 20 and 4 nm in the directions of the long and short axes, respectively, and the lattice fringe spacing was 0.39 nm (Figure 3a). This value is consistent with the value of the unit cell of copper nitride (0.38 nm) and indicates that the (100) plane was exposed along the long axis of the particle.

Figure 3b shows an image of a plate-like copper nitride nanoparticle with a diameter of approximately 40 nm viewed from vertical direction (defined as the *a*-axis direction). The power spectrum obtained by fast Fourier transformation of the image in Figure 3b revealed concentric light spots (Figure 3c). The $\langle 100 \rangle$ direction (angle brackets denote a family of directions such as [100], [010], or [001]) of copper nitride normally indicates a reciprocal lattice vector having a 90° angle between the *b*-axis and the *c*-axis in a concentric fashion because of cubic structure. In the power spectrum in Figure 3c, for brighter spots, two pairs of the spots arranged in a cross-shaped pattern were observed at a twist angle of 53° (*b* and *c* and *b'* and *c'*, respectively). The twist angle is an intrinsic angle for copper nitride crystal because of a lattice constant matching (see supplementary information). The direction for the edges of the nanoparticles was perpendicular to the direction of crystal growth. Although cursory inspection of the image suggests that the crystals grew randomly, in fact the copper nitride nanoparticles, which are preferentially grew to $\langle 100 \rangle$ direction, coalesced each other with the intrinsic angle for crystal growth. Selective growth to $\langle 100 \rangle$ direction was indicated by the sharpness of the (100) peak in the XRD pattern (Figure 1). On the basis of the XRD pattern and the electron microscopy images, we interpreted the shape of the copper nitride nanoparticles prepared from CuC10 to be plate-like.

An HAADF-STEM cross-section image of a copper nitride nanoparticle is shown in Figure 3d, and a magnified image and a crystal diagram viewed along the [011] direction is illustrated in Figures 3e and 3f, respectively. In Figure 3e, two types of contrast attributed to different atomic columns are clearly observed. We analyzed the columns by simulating the phase contrast and the atomic arrangements from a viewpoint in the [011] direction (inserts e1 and e2, respectively). We attributed the different contrasts to two types of Cu atomic columns, one with a large number of copper atoms (Cu A site) and the other with a small number of copper atoms (Cu B site). Furthermore, an indistinct border on the lower part of the atomic columns (indicated by the yellow arrow in Figure 3e) was observed and was attributed to twisting of a lattice facet.

4. Conclusions

We prepared plate-like copper nitride nanoparticles from a fatty acid copper(II) salt. The anisotropy ratio of the nanoparticles was estimated by analysis of the XRD pattern. High-resolution electron microscopy revealed that the plate-like nanoparticles grew selectively in the [100] direction.

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[13] Detailed procedures and manufacturers of reagents were described in the Supplementary Information.

Captions

Figure 1. XRD patterns of copper nitride samples prepared from CuC10 and CuC2.

Figure 2. TEM images of copper nitride nanoparticles prepared from (a) CuC10 and (b) CuC2.

Figure 3. HR-TEM images of copper nitride nanoparticles prepared from CuC10: (a) nanoparticle viewed from horizontal direction. (b) a 40-nm-diameter nanoparticle viewed from vertical direction; the axis directions (b, c, b', and c') were determined from the power spectrum shown in panel (c). (c) Power spectrum obtained from fast Fourier transform analysis the image in (b). (d) HAADF-STEM image of a copper nitride nanoparticle viewed from horizontal direction. (e) Enlarged figure of the area indicated orange rectangle in panel (d). (f) Crystal diagram of copper nitride.

Table 1. Estimated crystallite sizes from XRD peaks.

Figure 1.

Figure 2.

Figure 3.

Table 1.

Reagent	Estimated crystallite size (nm)			Crystallite size ratio relative to the (100) crystallite size	
	(100)	(110)	(111)	(110)/(100)	(111)/(100)
CuC10	15.7	10.3	5.4	0.656	0.344

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CuC2	29.9	25.6	24.1	0.856	0.806
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Graphical Abstract (for review)