SHORT COMMUNICATIONS

Preparation and Structure of Copper Nanoparticles-polysilane Composite Film

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Recently, the reaction of metal salts on a polymer surface have been investigated in detail for applications to produce new magnetic materials or to produce metallized plastic materials by reducing metal salts using hydrogen gas¹ or aminoboranes,² but polymers which can reduce metal salts have been only slightly reported.

Polysilanes are known to have a reductive nature for reducing noble metal salts or silver salts to form the corresponding noble metals by the high HOMO-electrons of the Si-Si σ -bonds.³ However, metal salts, which can be reduced by polysilanes, are limited in metals which have high standard oxidation potentials, *i.e.*, noble metal salts and silver salts, and reduction of metal salts having a low oxidation potential, such as copper (Cu) or nickel salts, into metals is considered to be impossible using polysilanes.⁴ In this study, we report a new procedure for the preparation of a Cu nanoparticles-polysilane composite film.

We examined poly(phenylhydrogensilane) (PPHS) as the matrix resin and three Cu(I) salts, Cu(OCOCH₃), CuCl, and CuBr.

A typical example is as follows. A thin film of PPHS (Mw: 11,000) on a plate was formed on a glass plate by the spin coating of a toluene solution of PPHS followed by drying at

140 °C under vacuum. The film-formed plate was dipped in an acetonitrile dispersion of a Cu(I) salt for 1–20 min under nitrogen at room temperature. When using Cu(OCOCH₃) as the Cu(I) salt, the color of the film slightly changed from colorless to black during the dipping. This film was rinsed with acetonitrile and dried at 140 °C under vacuum.

Figure 1. WAXD pattern of polysilane film preserved in a dispersion of copper(I) acetate; the diffraction peak at 2.10 Å is assigned to Cu(111).

Figure 2. Cross-sectional TEM images of Cu nanoparticles-polysilane composite films: (a) preserved in an acetonitrile dispersion of copper(I) acetate for 1 min; (b) 5 min; and (c) 20 min.

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In order to investigate the formation of metallic Cu, we observed the WAXD pattern of the obtained polysilane films. Concerning the film prepared with $\text{Cu}(\text{OCOCH}_3)$ as the Cu(I) salt, a diffraction peak is observed at $2.10 \text{ \AA}$, which is assigned to the (111) reflection of the metallic Cu (Figure 1).

Figure 2 shows TEM images of the cross-section for the obtained polysilane films preserved in an acetonitrile dispersion of $\text{Cu}(\text{OCOCH}_3)$ for 1 min, 5 min, and 20 min. In the film preserved for 1 min (Figure 2(a)), Cu nanoparticles are found in the upper half region, which is up to a $0.24 \mu\text{m}$ depth below the surface. The diameter of the copper particles is less than 10 nm. When immersed more than 5 min (Figure 2(b) and 2(c)), Cu nanoparticles are found in the entire film. As the immersion time increases, the composite film becomes thinner by the elution of polysilane in acetonitrile. In these three films, the concentration of the particles is so high and their outline is vague. Therefore, the size distribution of the Cu particles could not be measured.

In order to confirm the high reductive ability of **PPHS** in reducing $\text{Cu}(\text{OCOCH}_3)$, we investigated the reduction of Cu(I) salts using **PPHS** in a liquid phase. $\text{Cu}(\text{OCOCH}_3)$, CuCl ,

Figure 3. X-ray diffraction patterns of products from the reactions of **PPHS** with Cu(I) salts; (a) the Cu salt is $\text{Cu}(\text{OCOCH}_3)$; (b) CuCl ; and (c) CuBr .

Scheme 1. Possible mechanism of $\text{Cu}(\text{OCOCH}_3)$ reduction by **PPHS**.

and CuBr were used as the Cu salts. A typical procedure is as follows: In a flask, 0.11 g of **PPHS** was dissolved in 0.96 g of THF, and to this solution was added 0.50 mmol of the Cu(I) salt. The mixture was stirred at room temperature for 30 min. Only when using $\text{Cu}(\text{OCOCH}_3)$, the color of the mixture changed to black. The solvent was then removed by flowing nitrogen flow and the residual powder was obtained after drying under vacuum. The analysis of the products was carried out using the XRD technique (Figure 3).

$\text{Cu}(\text{OCOCH}_3)$ was reduced to Cu metal, and the Cu metal powder was partially oxidized. On the other hand, CuCl and CuBr were not reduced to Cu metal. These results revealed the selectivity of the counteranions of the Cu salts.

Taking into account the results mentioned above and the features of this reaction, we considered the mechanism as shown in Scheme 1 to be plausible for this reaction. Scheme 1 referred to the fact that hyper-coordinate hydrosilanes exhibit a higher reducing ability than the four-coordinate hydrosilanes to organic carbonyl or carboxyl compounds.⁵ In this mechanism, the acetate anion of $\text{Cu}(\text{OCOCH}_3)$ coordinates to the silicon atom of the hydrosilane to form the five-coordinate hydrosilane which is expected to have a stronger reducing ability than the starting four-coordinate hydrosilane species. The oxygen atom in the acetate anion has an especially high electronegativity and relatively low steric hindrance. Therefore, the acetate anion of $\text{Cu}(\text{OCOCH}_3)$ is expected to easily form a five-coordinate hydrosilane. The phenyl group in **PPHS** seems to stabilize the five-coordinate hydrosilane anion by electron de-

localization. The five-coordinate hydrosilane reacts with the Cu ion to form copper hydride (CuH). CuH reacts with another $\text{Cu}(\text{OCOCH}_3)$ to form the Cu metal and acetic acid. The rate-determining step of this mechanism is considered to be the formation of the five-coordinate silicon species in which the anion effect would be quite high. The strong anion dependence in the reaction corroborates the validity of this mechanism.

In conclusion, a new procedure for the preparation of a Cu nanoparticles-polysilane composite film was investigated. During the examination, we found that poly(phenylhydrosilane) (**PPHS**) exhibits an extremely high reductive ability for reducing $\text{Cu}(\text{OCOCH}_3)$. This technique can be used for the direct metallization of Cu on the polysilane film.

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