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Supercritical Hydrothermal Synthesis of Silicon-Functional Metal and Metal Oxide Nanoparticles

Takuya Ogawa,*[a] Manabu Furudate,[b] and Yoshito Oshima[b]

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A supercritical hydrothermal reaction was applied to synthesise silicon-functional metal and metal oxide nanoparticles. The Si-functionalised nanoparticles were formed by the hydrothermal reaction of metal salts and subsequent surface modification of the resultant particles by organofunctional silicon compounds. The metal salts studied were copper nitrate and acetate. Si-functionalised copper nanoparticles with a size below 10 nm were formed when an epoxy-functional silicone compound was used. The compositions, shapes and sizes of the resultant particles proved to be affected by the structures of the silicon compounds. As for the properties, the resultant particles were hydrophobic while nonfunctional particles were hydrophilic. This methodology can be potentially applied to the synthesis of Si-based nanohybrid materials in which such surface-modified nanoparticles are well dispersed in a polysiloxane matrix.

Introduction

Metal and metal oxide nanoparticles have been attracting considerable interest due to their unique properties including optical, electronic, magnetic and catalytic properties. Supercritical hydrothermal synthesis, SHS hereafter, seems to be one of the promising methods yielding metal oxide nanoparticles because of the following advantages: 1) it's a process without an organic solvent, 2) it gives the formation of small but highly crystalline particles and 3) it has quite a high reaction rate yielding a short process time.[1] Metal nanoparticles can also be synthesised by adding a reducing agent during the SHS process.[2–3] In addition, formation of hybrid nanoparticles having organic groups on the metal oxide surface has also been demonstrated by SHS and in situ surface modification.[2,4] These activities suggest that high temperature and pressure water including supercritical water are useful reaction conditions for the synthesis of nanometre sized particles.

On the other hand, we recently proposed a catalyst-free synthetic method for polysiloxanes by using high temperature and pressure water without an organic solvent.[5] This is based on hydrolysis of an alkoxysilane and subsequent polycondensation reactions yielding polysiloxanes. No acid catalyst is required for the method because water is acidic in nature at a temperature range between 250 and 300 °C.[6] Polysiloxanes thus formed have a large amount of silanol and methoxy groups on the backbone despite the high molecular weight.[5b] One can expect that these remaining groups work as interaction sites with other components including inorganic particles.

Combining the two high temperature water technologies described above seems quite feasible for yielding hybrid materials in which metal and/or metal oxide nanoparticles are well dispersed in polysiloxane as a matrix. Polymerisable organosilicon compounds with two, three or four alkoxy groups[7] on a silicon atom must be used for this purpose. To make this complex process simple, we report here, as an initial case, a one-pot synthesis of silicon-functional metal and metal oxide nanoparticles by using organofunctional silicon compounds with one alkoxy or a hydrolysable group that essentially do not undergo polymerisation yielding polysiloxanes but, instead, interact with the surface of the metal (oxide) particle. It can be expected that the sizes of the resultant particles are smaller than those without the silicon compound because of the particle growth suppression ability. In addition, the morphologies of the resultant particles are probably controllable by the process conditions and substrate structures. In the present study, copper nitrate and acetate were used as the metal salts for SHS because copper nanoparticles are highly attractive from the viewpoint of printable electronics.

Results and Discussion

1. Reaction of Various Si-Compounds with Copper Nitrate

Since SHS yields metal oxide particles in general, CuO particles were an essential product when a copper precursor

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[a] Business and Technology Incubator, Dow Corning Toray Co. Ltd.,
Ichihara 299-0108, Japan
Fax: +81-436-21-7617
E-mail: takuya.ogawa@dowcorning.com
[b] Department of Environment Systems, Graduate school of Frontier Sciences, The University of Tokyo,
Kashiwa 277-8563, Japan

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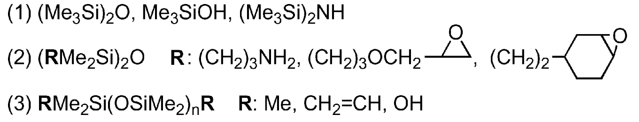
was used. One can, however, synthesise metallic copper particles by adding alkylthiols as reducing agents during the process.[2] Our synthetic strategy was as follows.

1) Identify suitable Si-compounds yielding Si-functional CuO particles

2) Examine reduction of Si-functional CuO to Si-functional Cu

The feasibility study was then conducted by using a reaction of an aqueous copper nitrate solution as a particle precursor and various Si-compounds as surface modification agents with the expectation that Si-functional CuO particles would be formed by in situ functionalisation. The Si-compounds examined in the present study are classified into three categories: (1) nonreactive reactants (2) organofunctional reactants and (3) polymeric reactants as listed in Scheme 1.



Scheme 1. Si-compounds examined in the present study.

Each solid product was first analysed by SEM to determine the shapes and sizes of the resultant particles. A section of the results is depicted in Figure 1.

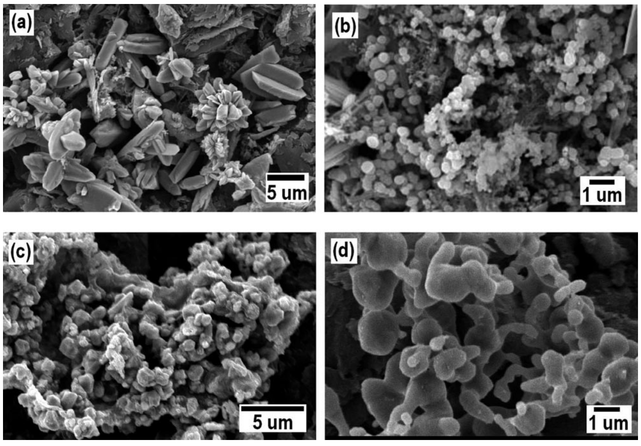


Figure 1. SEM micrograms of particles formed by SHS using $Cu(NO_3)_2$ and various Si-compounds: (a) and (b) silanol-terminated polysiloxane (c) 1,3-bis[2-(3,4-epoxycyclohexyl)ethyl]tetramethyldisiloxane (d) 1,3-diglycidoxypropyltetramethyldisiloxane.

The shapes and sizes of the particles were found to depend heavily on the structures of the surface modification agents. Runs with hexamethyldisiloxane, trimethylsilanol, trimethylsilyl-terminated polysiloxane and dimethylvinyl-terminated polysiloxane as the agent yielded particles being very similar to those using silanol-terminated polysiloxane (*OH-PDMS* hereafter) as shown in Figure 1 (a). The particles have a flower-like shape, the size of which is as large as 2 to 10 µm. This characteristic shape is essentially similar to that for particles synthesised without Si-compounds. This indicates that these Si-compounds had no (or very little) interaction with copper intermediate species such as $Cu(OH)_2$. This is consistent with the SEM-EDS results from which copper and oxygen were observed without evidence of silicon (not shown here). On the other hand, it is of interest to note that the run using *OH-PDMS* produced smaller sized spherical particles as depicted in Figure 1 (b) in an amount approximately 10–20% of the total. The sizes of the spherical particles were as small as 100 to 400 nm indicating that some degree of interaction between the copper intermediate and the silanol-terminated polysiloxane must have occurred thus suppressing the particle growth. In fact, a sign of silicon modification was evident from the EDS result. The products in these runs were black particles. They proved to be CuO (by an XRD analysis not shown here) regardless of the Si modification.

In contrast to the above results, runs with 1,3-bis[2-(3,4-epoxycyclohexyl)ethyl]tetramethyldisiloxane (*ECETMS* hereafter) and 1,3-diglycidoxypropyltetramethyldisiloxane (*GPTMS* hereafter) yielded dark red particles. This specific colour and the XRD profile as depicted in Figure 2 indicate that these products are metallic copper, not copper oxide. Hence, reduction of Cu^{2+} to Cu took place in the course of the series of hydrothermal and surface modification reactions. The reduction to Cu may be caused by an epoxy group as discussed later. As for the surface modification, the run with *GPTMS* yielded materials without silicon while that with *ECETMS* did produce Si-containing materials as shown in Figure 3. These results indicate that the product by the latter process consists of Si-modified particles. An epoxy group seems to be the surface modification site in the present reaction system. The observation that the product in the former did not contain silicon, as determined by the EDS analysis, may be explained if hydrolysis of an ether moiety in *GPTMS* occurred. It is notable that the particle shape of the former is very different from that of the latter as depicted in Figure 1 (c) and (d). The latter seems to be molten after generation from an aqueous salt solution. These two products are totally different from each other although the two were synthesised using epoxy-functionalised disiloxane. It can be concluded that the particle's morphology strongly depends on the structure of the surface modification agents.

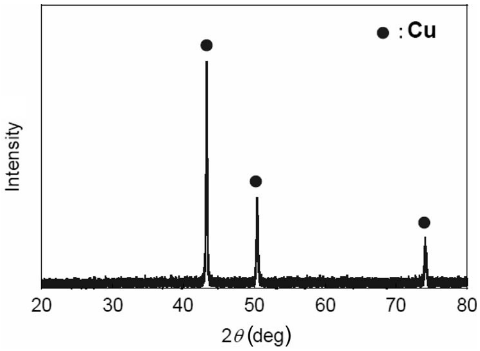


Figure 2. XRD profile of the synthesised particles obtained with *GPTMS*.

We also examined amine-forming and amino-functional Si compounds to see if an amino group is effective for surface modification. A run with hexamethyldisilazane yielded

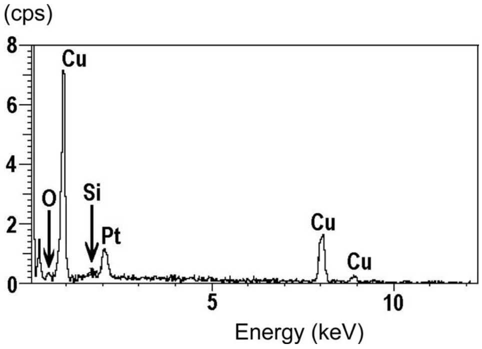


Figure 3. SEM-EDS spectrum of the red particles obtained with *ECETMS*.

a blue solution without forming a solid product. This may be interpreted as being the result of formation of a copper-amine chelate compound having high water solubility. The amine, ammonia in the present case, must be formed by hydrolysis of the disilazane under the reaction conditions. This indicates that silazane compounds are not suitable for SHS. On the other hand, a run with 1,3-aminopropyltetramethyldisiloxane gave a different result. The product was a mixture of heavy red particles and light white particles. According to a TEM analysis, the former was Cu with a size below 200 nm while the latter was polysiloxane spherical particles with a size about 1 µm or greater. This indicates that the amino-functional disiloxane yielded a solid despite the lack of a polymerisable group whereas reduction of the Cu cation to metallic copper probably took place. Salt formation between the amine and acetic acid yielding the solid material was suspected but the solid formed does not seem to be the acid/base salt. Although the polysiloxane particle formation is not fully understood, we can conclude that an amino-functional material is not appropriate for the surface modification.

2. In-Depth Morphological Characterisation by TEM

A TEM analysis was also conducted to gain insight into the in-depth morphological structures of the products. TEM micrograms of the particles synthesised with *ECETMS*, *GPTMS* and *OH-PDMS* are shown in Figure 4.

Although only micron-sized particles were observed by the SEM analysis, each product proved to contain particles, the sizes of which are below 20 nm. For example, the product in the run with *ECETMS*, particles with sizes between 500 nm and 1 µm, is major component as depicted in part (a) of Figure 4 but very small particles were observed as shown in part (b). According to the TEM-EDS mapping analysis of the small particles (not shown here), silicon was detected from the whole area as was copper, suggesting that these small particles are homogeneously modified by a Si-containing group. It should be emphasised that such smaller sized particles contain a higher content of silicon, according to TEM-EDS spectra, than the corresponding larger sized particles although the data are not shown here. This strongly suggests that particles formed by the in situ functionalisation method become smaller due to the surface modification by these Si-containing agents. This is consistent with the reported observations.[4c] It is also of interest that each Si-containing nanoparticle shown in Figure 4 (a, c, d) is composed of crystalline and amorphous particles. The degree of crystallinity may be dependent on the degree of modification by Si-containing molecules.

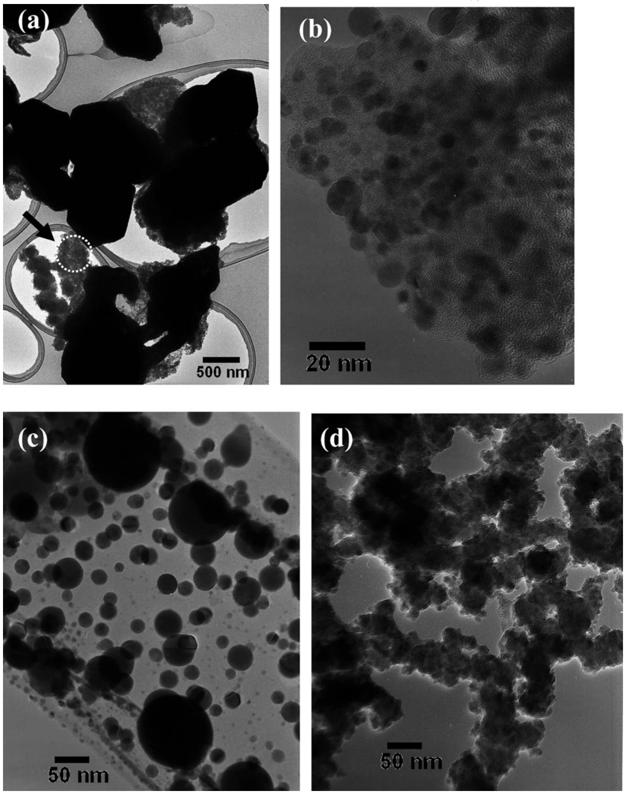


Figure 4. TEM micrograms of particles formed by SHS using $Cu(NO_3)_2$ and various Si-compounds: (a) and (b) *ECETMS*; (b): expanded microgram of the particles indicated by an arrow in microgram (a); (c) *GPTMS*; (d) *OH-PDMS*.

Based on the feasibility study, we selected *ECETMS* as a surface modification agent. Studies reported below were conducted in the presence of this epoxy-functional disiloxane.

3. Effect of the Amount of ECETMS on the Product

The effect of the amount of *ECETMS* on the particle formation was studied by various methods. First, ability of the resultant particles to disperse between water and chloroform was examined in order to understand how the amount of *ECETMS* affects the surface properties of the particles. The results are summarised in Table 1.

Red particles were formed in each run indicating that reduction of CuO to Cu had taken place. The higher the amount of *ECETMS*, the larger the quantity of particles in the organic phase indicating that the degree of surface modification of the particle gradually increases by increasing the amount of *ECETMS*. In the run with an amount of 20, all particles were in the organic phase.

Table 1. The effect of the amount of *ECETMS* on the copper particle formation.[a]

[ECETMS][b]	Amount of particles in each phase Aqueous	 Interface	 Organic
2	red (+++)	red (+++)	red (+)
5	red (++)	red (++)	red (++)
10		red (++)	red (+++)
20			red (+++)

[a] Temperature/pressure/time: 400 °C/30 MPa/5 min. Concentration of copper nitrate: 0.1 $\mathrm{mol\,L^{-1}}$. [b] The amount is defined as the [*ECETMS*]/[copper] weight ratio. The ratio of 10 corresponds to a [Si]/[Cu] molar ratio of 4.2.

According to an SEM analysis, the particle's shape proved to be independent of the amount of *ECETMS*. On the other hand, the particle size did depend, to some extent, on the amount of *ECETMS*. The number of smaller particles with a size below 100 nm increases with an increasing amount of *ECETMS* probably due to suppression of the particle growth by the surface modification agent. Larger particles with a size above 1 µm are, however, still present in the product. In fact, the particle size distribution is quite large: from about 100 nm to 1.5 µm. Silicon was detected by the SEM-EDS analysis for particles formed in runs with amounts of 10 and 20 for the *ECETMS*. In addition, several absorption bands assignable to Si–O–Si, Si–CH$_3$, methylene and OH groups were observed in the IR spectra for these Si-containing particles. The formation of small particles with sizes below 10 nm with a high content of silicon was observed by TEM and TEM-EDS analyses.

These results indicate that the degree of surface modification increases by increasing the *ECETMS* amount. An *ECETMS* amount of 10 or greater seems to be preferable for achieving sufficient surface modification. It was also indicated that the surface modification was not homogeneous, thereby yielding both large particles with low surface modifications and small particles with high surface modifications. The large particles are highly crystalline while the very small particles seem to be amorphous.

4. Effect of the Cu Salt Concentration

It has also been demonstrated that the salt concentration is another key factor controlling the particle size in SHS.[1] The lower the concentration, the smaller the particle size in general. SHS with copper nitrate in the absence of *ECETMS* did not yield a solid product due to the high solubility of the resultant particles in aqueous nitric acid. Hence, the reaction without *ECETMS* was conducted using copper acetate as a particle precursor. Products formed by the SHS without the surface modification agent are depicted in Figure 5. The particle size became much smaller by reducing the substrate concentration from 0.1 to 0.01 $\mathrm{mol\,L^{-1}}$. In fact, the sizes are 0.5–2 µm for the former and < 100 nm for the latter. As oxygen was detected by the SEM-EDS (not shown here) and the colour of the product was brown, the products in the present study are likely to be a mixture of Cu and Cu$_2$O as reported by Ziegler.[2]

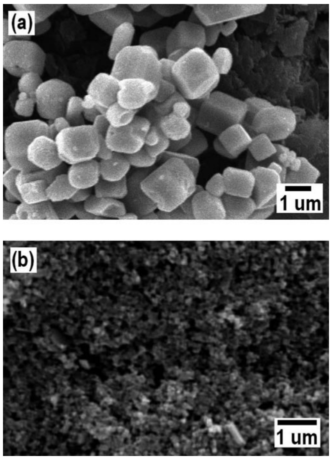


Figure 5. SEM microgarms of particles formed by SHS using different concentrations of copper acetate solution at 400 °C/30 MPa/5 min. (a): at 0.1 $\mathrm{mol\,L^{-1}}$; (b): 0.01 $\mathrm{mol\,L^{-1}}$.

SHS in the presence of *ECETMS* was carried out as the next step with a various concentrations of copper nitrate. The results are summarised in Table 2.

Table 2. The effect of the copper nitrate concentration on the cupper particle formation.[a]

[Cu(NO$_3$)$_2$][b]	Amount of particles at each phase Aqueous	 Interface	 Organic
0.01		red (+)	red (++)
0.05		red (+)	red (++)
0.1		red (++)	red (+++)
0.2		dark red (++)	dark red (+++)

[a] Temperature/pressure/time: 400 °C/30 MPa/5 min. The *ECETMS* amount: 10 times that of the calculated Cu amount. [b] The copper nitrate concentration in $\mathrm{mol\,L^{-1}}$.

Each product was dispersed into the organic phase and at the interface suggesting that the particles' surfaces became hydrophobic as was expected. It was demonstrated by SEM and TEM analyses that the shapes and sizes of the products were not affected by the salt concentration. In fact, both large and very small particles, the sizes of which are above about 500 nm and below 10 nm, respectively, were formed in each run. The formation of large particles must be due to the high solubility of CuO particles as an intermediate for metallic copper particles. Sue and co-workers have reported that the particle sizes of metal oxides derived from metal nitrates by SHS strongly relates to the solubility of the metal oxide at the examined temperature. CuO has the largest particle size among several metal oxides due to the highest solubility.[8]

Silicon was detected by the SEM-EDS analysis for the products synthesised at concentrations of 0.1 and 0.2 $\mathrm{mol\,L^{-1}}$. This indicates that a higher nitric acid concentration is preferable for the surface modification in the present study. This may be attributable to a higher degree of hydrolysis of the epoxy group of the *ECETMS* being necessary for the surface modification. It should be noted that the product derived from a 0.2 mol L^{-1} Cu(NO$_3$)$_2$ solution was discernibly dark-coloured while the other three products were red particles. It was speculated that: (1) the degree of surface modification increases as the Cu salt concentration increases, (2) an oxide surface on the Cu, the colour of which is dark red or black, is required for surface modification. If this second assumption is true, particles with a higher degree of surface modification become dark red.

5. Quantitative Analysis of Si-Containing Organic Groups of Si-Functional Copper Particles

Thermal weight loss was examined in order to have quantitative information about the degree of functionalisation of Si-functional particles. The weight loss profiles of the two Si-functional particles by thermogravimetric analysis are depicted in Figure 6.

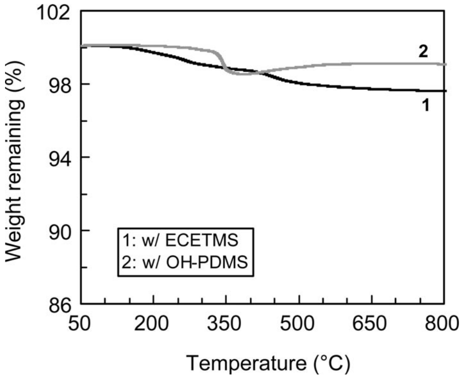


Figure 6. The weight loss profiles of the two Si-functional particles synthesised with 1) *ECETMS* and 2) *OH-PDMS*.

The copper particles synthesised with *ECETMS* exhibited an essentially two step weight loss. The first step, below approximately 300 °C occurs with a loss of about 1% while the second step ranged between about 300 and 500 °C also with the loss of about 1%. The cause of the two step weight loss has not been identified but both steps can be attributed to loss of organic components from the Si-functional particles. On the other hand, the particles yielded in the presence of *OH-PDMS* proved to be copper oxide as described above. They exhibited a sharp weight loss at about 350 °C and a gradual weight gain above about 400 °C. The weight gain can not be well interpreted but is probably due to thermal oxidation of the particles being partially-reduced to Cu$_2$O particles during heating. The observed sharp weight loss is in striking contrast to the weight loss profile of the particles synthesised with *ECETMS* indicating that these two materials degrade by a different pathway. The observed sharp weight loss is a characteristic profile for linear polysiloxanes.[9] This is consistent with the speculation that the product synthesised in the presence of the *OH-PDMS* has a linear siloxane polymer on the particle surface. It can be concluded that both particles have organic groups on the surface with the degree of functionalisation ranging between about 1 and 2 wt.-%. These values are much lower than the loaded amount i.e. 10 times that of the calculated Cu amount.

An XPS analysis was also carried out to gain insight into the top surface of the functionalised particles synthesised with *ECETMS*. Since the binding energy for Cu2p3/2 was 933 eV, i.e very close to the Cu's authentic value of 932.8 eV, the surface is copper, not copper oxide as was demonstrated by the XRD result described in section 1. According to the [C]/[O]/[Si]/[Cu] atomic composition data, the surface group will essentially be the same as the loaded disiloxane's structure without discernible degradation during synthesis. This is consistent with an estimated surface modification mechanism described in the next section. It was also suggested from the composition data that one Si-containing group is attached to every two or three surface Cu atoms, on average.

6. The Surface Modification Reaction Mechanism for the SHS Using ECETMS

The reaction of aqueous copper nitrate and *ECETMS* yields both solvent-soluble and insoluble materials. Because structural characterisation of the insoluble material is not easy, the soluble product was analysed by ^{29}Si and ^{13}C NMR spectroscopy to elucidate the surface modification reaction mechanism. It is expected that the soluble product is composed of a desired reaction product and degraded *ECETMS*, because a quite small portion of the loaded *ECETMS* was used for the surface modification reaction as suggested by the thermogravimetric analysis. Since it is thought that the structure of the molecules combined at the Cu particle surface of the insoluble product is similar to that of the soluble product, one may be able to estimate the structure of the Si-containing group on the surface of the insoluble particle by the NMR analyses although the spectra are not shown here.

Taking the NMR spectroscopic results into account, the reactions summarised below possibly take place by the present in situ surface modification process in the SHS.

1. An epoxy group of *ECETMS* undergoes hydrolysis to yielding a diol function.
2. The hydroxy group thus formed is oxidized to an give an aldehyde or a ketone.
3. A siloxane bond of *ECETMS* partially undergoes hydrolysis to yield a silanol group.
4. A part of Si–C linkages degrades to yield Si–O–*Si*–OH and Si–O–*Si*–O–Si linkages. This may be due to thermal degradation because the Si–C linkages are hydrolytically stable.
5. Degradation species are formed by the above reactions 1 and/or 2 and react with the copper particles' surfaces to achieve surface modification.

The copper particles' surfaces are probably modified by a dehydrative condensation reaction between a hydroxy group formed by hydrolysis of an epoxy group and a surface hydroxy group of the particles. In fact, trimethylsilanol and hexamethyldisiloxane, both of which generate an Si–OH group during SHS, did not yield the surface-modified particles indicating that an Si–OH group does not function as a reactive site. In addition, it can be deduced that oxidation of the hydroxy group, which is not used for the surface modification, to an aldehyde or a ketone group results in reduction of copper oxide particles, which were formed at an early stage of the SHS, to metallic copper.

Conclusions

Synthesis of Si-functional copper particles by in situ surface modification during SHS was conducted by a batch process using copper precursors and various Si-containing compounds as surface modification agents. The study indicates that Si-functional copper particles are accessible by a reaction of aqueous copper nitrate and an epoxy-functional disiloxane at 400 °C and 30 MPa. It is interesting to note that reduction of copper oxide to metallic copper occurred during the SHS presumably by the action of the epoxy group under the reaction conditions.

The product was composed of large particles with sizes ranging from between 0.5 and 1.5 µm and very small particles below 10 nm. In other words, the particle size distribution of the product was quite large. The possible reason for this large size distribution must be the long reaction time and the high solubility of copper oxide in high temperature water. In fact, it isn′t easy to control the particle size using the present process. A synthetic process with rapid heating followed by immediate formation of a particle core should work to yield smaller-size particles with a narrow size distribution.[1]

The TEM-EDS analysis indicates that the larger size particles are essentially copper without or with a very low degree of surface modification whereas the particles as small as 10 nm or smaller proved to be modified by an Si-containing group. The formation of such small particles is likely to be caused by the surface modification that suppresses the particle growth. Studies of how the morphology can be controlled are in progress.

Experimental Section

Equipment: A reactor with an internal volume of 5 mL was made of 3/8” stainless steel SUS 316 BA pipe. Connectors were Swagelok products. A salt bath with a temperature deviation within ±1 °C was used as a heat source.

Materials and Characterisation Methods: Trimethylsilanol, the four disiloxanes, hexamethyldisilazane and the three polysiloxanes as surface modification agents were used without further purification. Trimethylsilanol was a reagent from Chisso while other Si-containing materials were Dow Corning intermediates.

^{29}Si and ^{13}C NMR spectra in CD_3COCD_3 solution were recorded using tetramethylsilane as an external standard with a Bruker AC300P spectrometer. Chromium acetylacetonate [$Cr(acac)_3$] was used as a relaxation agent for the ^{29}Si NMR analysis.

SEM-EDS analyses were carried out with an accelerating voltage of 15 kV using a JEOL JSM-5600 microscope attached to an Oxford Instruments Link ISIS spectrometer. The specimen was prepared as follows: a dispersion of each powder sample in acetone was dropped on a sample stage (made of either carbon or brass) using a micropipette and dried at ambient temperature in the atmosphere. The powder was then coated with platinum by using a Sanyu Electron SC-701 vacuum deposition system to provide an analytical specimen.

TEM-EDS analyses were conducted with a JEOL JEM-2010F microscope attached to an Oxford Instruments Link ISIS spectrometer. The observations were made at an accelerating voltage of 200 kV. The specimen was prepared by the procedure similar to that for SEM-EDS but without the Pt coating process. A microgrid made of either molybdenum or copper was used for the analysis.

FTIR spectroscopic analyses were performed with a Thermo Scientific Nicolet 4700 instrument with an ATR accessory by a SENSIR Technologies DuraSampl IR II.

XRD profiles were recorded with a monochromator in air with a MacScience M03X instrument. A glass sample stage was used and the measurement conditions are summarised as follows: X-ray generator voltage: 3 kW; target: 1.54056 Å (Cu-K_α); voltage: 35.0 kV; current: 20.0 mA; sampling width: 0.02 °; scanning speed: 3.0 ° min^{-1}; divergence slit: 1.00 °; scattering slit: 1.00 °; receiving slit: 0.30 mm.

The thermogravimetric analyses were conducted with an SII TG-DTA320 instrument at a heating rate of 10 °C min^{-1} under a 2% H_2/N_2 mixed gas atmosphere. The atmospheric gas flow rate in each run was 200 mL min^{-1}.

An X-ray fluorescence analysis (XRF hereafter) was conducted with a PANalytical Axios instrument after preparation of aqueous copper solutions for calibration. Each sample solution was prepared by adding nitric acid to an aqueous solution of the reaction product, after filtration with a PTFE membrane with a diameter of 0.2 µm, in order to adjust the acid content to 0.1 mol L^{-1}. The standard copper solution for the present analysis was prepared by dilution of a Kanto Chemical Cu-100 aqueous solution (with a copper content of 100 ppm) with ultrapure water purified with a Millipore Direct-Q model purifier to yield 1, 5 and 10 ppm copper solutions. The copper ion concentration was quantitatively analysed and the values were converted into the conversion of metal salt to Cu particles.

XPS analysis was performed at 10^{-7} Pa with a Shimadzu ESCA-3400 instrument with an Mg-K_α X-ray source.

Synthesis of Hybrid Copper Particles as a Typical Example: A copper nitrate aqueous solution with a concentration of 0.05 mol L^{-1} (1.76 mL; 0.09 mmol of [Cu]) and *ECETMS* (0.07 mL; 0.38 mmol of [Si]) were placed in a one-end capped reactor attached to a thermocouple and the other end was then sealed. Since the concentration of copper nitrate is low and the amount of the nonvolatile Si compound is small, we assumed that the reactant is just water. The intended pressure inside the reactor based on the assumption was 30 MPa. The reactor was placed in a preheated salt bath at 400 °C to start the reaction as schematically depicted in Figure 7. The temperature profile during heating is shown in Figure 8. After heating for 5 min, the reactor was removed from the salt bath and the contents poured into a water bath to terminate the reaction. Solid and liquid products were recovered in a test tube by using water and dichloromethane. The distribution of the solid product to both organic and aqueous layers was examined by shaking the test tube.

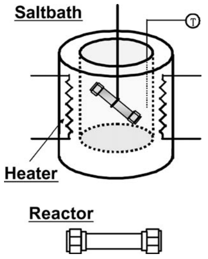


Figure 7. Reaction system in the present study.

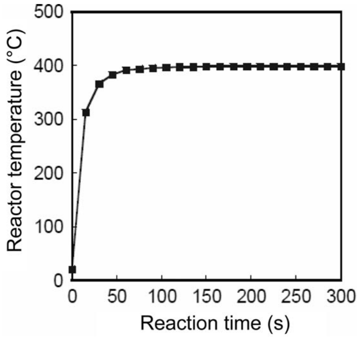


Figure 8. The temperature profile during heating at 400 °C.

Solid Product: The solid product separated from the mixture by centrifugation was washed three times with acetone. The reddish brown product was finally dried at 80 °C in vacuo. XPS data [eV]. Cu2p3/2: 933.0; Cu2p1/2: 952.8; Si2p: 102.9; O1s: 532.6. The [C]/[O]/[Si]/[Cu] atomic composition: 59.5/17.6/6.4/16.5.

Liquid Product: A liquid product was obtained by removal of dichloromethane under reduced pressure.

Conversion of the Copper Salt to Metallic Copper: In order to realise an anion's effect, a reaction product derived from copper acetate was also examined. Based on the XRF, each conversion value was higher than 99.5%. Since the run with copper nitrate yielded a slightly higher value than that with acetate, copper nitrate was used as the Cu source in almost all of the present study.

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