Paper

Silica Coating of Copper Nanoparticles by a Fast and Facile Microwave Method

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SYNOPSIS

A rapid process of silica coating of colloidal copper nanoparticles by microwave method was studied. Copper nanoparticles were prepared from CuCl_2 aqueous solution using hydrazine as reducing agent and cetyltrimethylammonium bromide and citric acid as stabilizers. Obtained copper nanoparticles having the mean diameter of around 30 nm were surface-treated by 3-aminopropyltriethoxysilane and then surface-coated with silica using tetraethoxysilane or silanol terminated polydimethylsiloxane as silica precursors. The uncoated and silica coated copper nanoparticles were characterized by UV-Vis spectroscopy, transmission electron microscopy, X-ray photoelectron spectroscopy and X-ray diffraction measurements. By varying several conditions, Cu nanoparticles could be coated with uniform silica shell with the reaction time, i.e. the microwave irradiation time, of only 5 min, although single core containing core-shell nanoparticles could not be obtained. Conclusively, this microwave method is one of the green processes for its short reaction time.

KEY WORDS

core-shell, microwave method, surface plasmon resonance, X-ray diffraction

1 Introduction

In recent years, research has been directed towards the synthesis and application of noble metal nanoparticles owing to their potential applications in such fields as catalysis, biology, electronics, and information technology compared to bulk metals¹⁻⁵. Among the different noble metal particles, Cu is the most abundantly used metal in electronics applications due to its high conductivity and low cost. In addition, Cu nanoparticles have potential applications as a catalyst for various transformations including water-gas shift and gas detoxification⁶, and as an electrocatalyst in solid-oxide fuel cells^{7,8}. It is well-established that noble metal nanoparticles, in particular, Ag and Au, support plasmon resonances that can be tuned throughout the UV-Vis-NIR region^{9,10}. In addition, the plasmonic properties of Pt and Pd nanodisk arrays fabricated by the hole-mask lithography were found to exhibit localized surface plasmon resonance (LSPR) that are broader and weaker than Ag¹¹. The requirement for LSPR is a large negative real and small imaginary dielectric function, thus other metals such as Cu meet this criterion and in theory should support plasmon resonances for at least part of UV-Vis-NIR region^{12,13}. Another important

application of Cu nanomaterials is their potential use for surface enhanced Raman scattering (SERS), whose enhancement factor is dependent on the strength of the local electric field and the nature of the material¹⁴. However, the plasmonic properties of Cu have not received much attention as compared to Ag and Au. This is mainly because Cu nanostructures are prone to fast oxidation and, consequently, are hard to synthesize chemically. The dominant product of the surface oxidation of Cu is Cu_2O and the minor product is CuO ¹⁵. A number of different ways have been developed in order to prevent oxidation of Cu nanoparticles and to study their optical properties^{16,17}. The reported methods include stabilization of the nanoparticle during their synthesis such as chemical reduction of Cu(II) ions in aqueous solution in the presence of various capping agents such as cetyl-trimethylammonium bromide (CTAB)^{15,18}, ethylenediamine (EDA)¹⁹, polyvinylpyrrolidone (PVP)²⁰ and sodium dodecylbenzene sulphonate (DBS)²¹. In addition, Pileni and her research group demonstrated the size and shape controlled synthesis of Cu nanoparticles by a method using reverse micelles as a template²². Furthermore, Lisiecki and Pileni synthesized Cu nanoparticles with sizes of 2–10 nm by varying the

water content, the concentration of reducing agent, or the salt concentrations in AOT-water-oil reverse micellar systems²³. In the second, commonly used method of stabilization is to prepare the Cu nanoparticles in organic solvents by decomposing or reducing various Cu complexes in the presence of capping agents^{24–26}. However the use of such organic compounds is harmful and hazardous.

Silica coating is one of the most widely used methods for the surface modification of nanoparticles (NPs)^{27,28}. It has a number of advantages over the organic coating of NPs. Silica acts as a robust and inert layer against the degradation of optical properties and imparts water dispersibility. This coating method can introduce a cross-linked silica shell to protect the core NPs from the external environment^{29,30}.

To the best of our knowledge, coating of colloidal Cu nanoparticles with silica to form core-shell nanoparticles was first demonstrated by Kobayashi et al.³¹ The method of coating by Kobayashi is relatively time consuming and costly and the results showed that all the Cu cores were not well coated by silica. In addition, it is well known that during the coating of CTAB capped nanoparticles, the concentration of CTAB surfactant must be closed to critical micelle concentration³². However, large amount of CTAB in the system makes the displacement of silane coupling agent difficult due to strong binding of CTAB molecule to the nanoparticle surface. Thus, with the CTAB-based approach it has been a challenge to develop effective methods to coat Cu nanoparticles with uniform silica within short reaction time³².

Here, we present a facile and fast approach to deposit silica on Cu nanoparticles using a novel microwave (MW) method. The advantage of this process is simply to speed up the hydrolysis and condensation of silica precursor by MW irradiation to form silica layer around all Cu nanoparticles to avoid their oxidation. The tunable optical properties of silica coated Cu nanoparticles with different shell thickness are also revealed simply by changing the concentration of silica precursor. Previously we have successfully coated Ag and ZnO nanoparticles with silica using MW method^{33,34}. However, silica coating of Cu nanoparticles showed tremendous difficulty of stability of core particles during coating process compared to the other nanoparticles. To find the suitable conditions for preparing silica coated Cu core-shell nanoparticles, two kinds of silica precursors, tetraethoxysilane (TEOS) and siloxane terminated polydimethoxysilane (SPDMS), were used.

2 Materials and Methods

2.1 Materials

Copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), cetyltrimethylammonium bromide (CTAB), hydrazine monohydrate, tetraethoxysilane (TEOS, 99.9 %), sodium hydroxide (NaOH) and ethanol (99.5 %) were purchased from KANTO Chemical Co. Inc. 3-Aminopropyltriethoxysilane (APTES) was purchased from Tokyo Chemical Industry Co. Ltd. Citric acid (CA, >99 %) was purchased from Sigma-Aldrich, USA. Silanol terminated polydimethylsiloxane (SPDMS) with molecular weight 400–700 was supplied by Gelest Inc. All chemicals were used without further purification. Milli-Q water was used in all the preparations.

2.2 Methods

2.2.1 Synthesis of Cu nanoparticles

The Cu nanoparticles were synthesized by following Kobayashi's method³¹ using CTAB and CA as stabilizers. Hydrazine monohydrate was used as reducing agent. In a typical synthesis, freshly prepared 10 ml of 0.20 M hydrazine aqueous solution containing 3.0×10^{-3} M CTAB and 5.0×10^{-4} M CA was added to 10 ml of 2.0×10^{-3} M CuCl_2 aqueous solution containing 3.0×10^{-3} M CTAB and 5.0×10^{-4} M CA under vigorous stirring at room temperature. The formation of Cu nanoparticles was confirmed by changing the colour of the mixture to red.

2.2.2 Silica coating of Cu nanoparticles

Silica coating of Cu nanoparticles were carried out by following modified Stöber method using effective MW irradiation. The MW synthesis was performed using a commercial microwave apparatus, Shikoku Keisoku SMW 064. This system has the frequency of 2.45 GHz and maximum power of 500 W. A built-in magnetic stirring system was used to carry out the agitation and an optical fiber sensing system was used to measure and control the reaction temperature during the synthesis. The fiber was directly inserted into the reaction solution. According to our previous report³³, the MW power was adjusted to 30 %–50 % of maximum power to avoid particle aggregation.

The schematic illustration of silica coating of Cu nanoparticles by MW method is shown in Fig. 1. To a 20 mL colloidal solution of CTAB stabilized Cu nanoparticles, a freshly prepared APTES (200 μL , 1.0 mM) was added with strong magnetic stirring. The mixture of APTES and Cu was allowed to stand for 15 min to ensure the complete complexation between the amino groups of APTES and Cu nanoparticles surface. TEOS/SPDMS was then added followed by the addition of NaOH (1 mL 0.10 M) as a catalyst to speed up the hydrolysis and condensation of TEOS/SPDMS. The reaction mixture was then immediately MW irradiated at 50 °C for 5 min. Excess APTES, TEOS/SPDMS and NaOH were then separated by centrifugation

Fig.1 Schematic illustration of silica coating of Cu nanoparticles by MW method.

at 9500 rpm for 15 min. The supernatant was discarded and the silica coated Cu nanoparticles (Cu@SiO_2) were dispersed in water or ethanol.

3 Characterization methods

Transmission electron microscopic (TEM) images were obtained with JEM 2010 (Jasco, Japan) operating at 200 kV. The samples were prepared by dropping and evaporating the particle suspension onto a carbon-coated copper grid. Average particle sizes were measured from several TEM images and size distribution was obtained by measuring over 100 particles in an arbitrary chosen area of a TEM image. Absorption spectra were measured with a UV-Vis spectroscopy (V-560, Jasco Corp., Japan). The X-ray photoelectron spectroscopy (XPS) measurements were performed with ESCA 5600 (ULVAC PHI Inc., Japan) using a Mg $\text{K}\alpha$ X-ray source operating at 200 W (15 kV). The base pressure in the analysis chamber was kept under 1×10^{-7} Pa during XPS measurements. Binding energies were referenced to the adventitious C 1s peak at 284.8 eV. X-ray powder diffraction (XRD) patterns were obtained on a Rigaku RINT 2100 diffractometer using Cu $\text{K}\alpha$ radiation with operating parameters as follows: 200 mA, 40 kV, 2 θ scanning from 20° to 80°. Before the measurements of XPS and XRD, the colloidal nanoparticles were centrifuged and dried under vacuum at 80 °C for 24 hrs.

4 Results and discussion

4.1 Synthesis of Cu nanoparticles

The size and morphology of the prepared uncoated Cu

Fig.2 TEM images of uncoated Cu (a), and silica coated Cu nanoparticles with TEOS loading of 5.0 mM (b) and 10 mM (c).

nanoparticles were interpreted from transmission electron microscopic (TEM) photograph. Fig. 2 (a) depicts a corresponding TEM image of the native Cu nanoparticles. The micrograph shows that synthesized Cu nanoparticles are in spherical morphology. The particle size was estimated by measuring hundreds of particles in TEM image and taking the averages of them. The particle size of uncoated Cu nanoparticles was found to be 30 ± 10 nm. The typical colour of the colloidal Cu was red. It was observed during the synthesis of Cu nanoparticles that continuous stirring of the mixture after addition of reducing agents resulted in the aggregation of the particles. This was confirmed by the color change from red (stable colloidal Cu) to black (aggregated Cu particles). Therefore, reducing agent was added into the Cu precursor solution with strong magnetic stirring and then the solution was kept unstirred for 3 hrs at room temperature to ensure the completion of the reaction.

4.2 Silica coating of Cu nanoparticles

The Cu nanoparticles were coated with silica that (i) improve the stability of nanoparticles by reducing aggregation, (ii) improve the stability of the particles against the surface oxidation, and (iii) allow for further modification of the nanoparticle surface. TEM images of the prepared Cu@SiO_2 particles are shown in Figs. 2 (b) and (c). Darker and lighter parts of the particles correspond to Cu and silica, respectively. This is due to the fact that the atomic mass of Cu and then the electron density are higher than that of Si. It can be seen from the TEM images that all the Cu nanoparticles were coated with uniform silica shell. However, single-core containing core-shell Cu@SiO_2 was not observed in the present study. This might be that the Cu nanoparticles tend to aggregate prior to the generation of silica shell around the particles. In addition, the parameters such as water concentration, TEOS/SPDMS concentration and NaOH concentration were not optimized in this study. Research in this direction is in progress.

4.3 Effect of CTAB concentration on silica coating

Silica coating of Cu nanoparticles prepared with different CTAB loading was carried out by MW method. We found that low concentration of CTAB during Cu nanoparticle synthesis resulted in aggregation. With high concentrations of CTAB in system and the associated equilibrium between CTAB in solution and that on the surface of nanoparticles, it is difficult to deposit a uniform silica shell onto the surface of the nanoparticles³⁵. Therefore, fixing the concentration of CTAB during the preparation of Cu nanoparticles as well as their silica coating was very crucial. We observed that comparatively better silica coating of Cu nanoparticles could readily achieved simply by keeping the CTAB concentration at 3.0×10^{-3} M during Cu nanoparticle synthesis (Fig. 3). At the CTAB concentration higher than 3.0×10^{-3} M, besides core-shell structure, gel-like structure and core free silica were observed.

Silica coating also was performed by using two different kinds of silica precursors, TEOS and SPDMS. It was found that better silica coating resulted with TEOS. This is due to the fact that TEOS was easily hydrolyzed and condensed to deposit silica on Cu nanoparticles. When SPDMS was used as precursor, core-shell structure was rarely found and the large amount of gel-like structure was observed (Fig. 3(c)).

4.4 Comparison of optical properties

Extinction (UV-Vis) spectra of silica coated Cu nanoparticles are shown in Fig. 4. Data shows that the surface plasmon band of Cu nanoparticles shifted towards red after silica coating³³. In addition, blue shifting was also observed with thicker silica shell³³. These general observations are consistent with data previously published³³. This red shift of the surface plasmon resonance was due to the increase in local refractive index around particles. The refractive index of silica is slightly higher than that of water³³. Therefore, shift of the plasmon band toward red in coated samples indicates that Cu nanoparticles were

Fig.3 TEM images of silica coated Cu nanoparticles prepared by MW technique with TEOS and high CTAB loading (a), with TEOS and low CTAB loading (b), and with SPDMS and low CTAB loading (c).

coated with silica.

4.5 Crystal phase analysis of uncoated and silica coated Cu nanoparticles

Fig. 5 (a) depicts the XRD pattern of uncoated Cu nanoparticles, whereas Figs. 5 (b) and (c) represent those for Cu@SiO₂ nanoparticles. The pattern for uncoated Cu (Fig. 5 (a)) was measured a day after the preparation of particles. The XRD patterns of Cu@SiO₂ samples shown in Figs. 5 (b) and (c) were measured after 1 week and 1 month, respectively. The XRD patterns of uncoated and Cu@SiO₂ nanoparticles showed peaks at 43.6° and 74.2° which were attributed to those of metallic Cu (JCPDS card No. 4-0836). Besides the metallic Cu peaks, several peaks assigned to Cu₂O (JSPDS card No. 5-0667) were strongly detected at 36.7, 42.4, 61.7° in uncoated Cu samples (Fig. 5 (a)). This

Fig.4 Extinction spectra obtained from aqueous dispersion of the uncoated and silica coated Cu nanoparticles with TEOS loading of 0.0 mM (a), 5.0 mM (b), 10 mM (c), and 20 mM (d) prepared by MW technique. Spectra have been arbitrarily displaced on the vertical axis to better illustrate the subtle silica-thickness-dependent shift of the plasmon band. The wavelength at which the respective band maxima occur is also shown.

Fig.5 XRD patterns of uncoated Cu nanoparticles (a) and silica coated Cu nanoparticles 1 week (b) and 1 month (c) after the preparation.

XRD result and the UV-Vis spectra (Fig. 4) indicate that many Cu nanoparticles, which were stable in the colloid solution, were oxidized in air after sample preparation for XRD measurements by drying. The XRD pattern of Cu@SiO₂ nanoparticles did not change even after 1 month of sample preparation. This indicates that the silica coating prevents the Cu nanoparticles from oxidation even in air.

4.6 Surface analysis of the uncoated and silica coated Cu nanoparticles

XPS is an important surface sensitive analytical technique useful for the identification of elements presents on the surface of the nanoparticles. It also gives the information about the oxidation state of Cu nanoparticles. Fig. 6 depicts the survey scan spectra of uncoated and silica coated Cu nanoparticles. The survey scan of the surface of Cu nanoparticles after silica coating showed the addition of Si 2p. In addition, no peak corresponding to Cu 2p was observed after silica coating which revealed that all Cu nanoparticles were coated with silica. This is in good agreement with TEM results (Fig. 3 (b) and (c)). It should be mentioned that XPS data were taken after 1 month of preparation of silica coated sample. This result also proves the stability of Cu nanoparticles after silica coating.

5 Conclusions

In summary, a simple and fast synthesis method for silica coating of Cu nanoparticles was presented by using colloidal Cu and TEOS/SPDMS as silica precursors, APTES as surface primer, and NaOH as the catalyst. Compared to the conventional methods which take a few hours to several days, the present method takes only 5 min to encapsulate the Cu nanoparticles with silica. The obtained silica coated Cu nanoparticles exhibited a change in surface plasmon resonance absorption, which confirmed the silica coating of Cu nanoparticles. XRD results revealed the long term stability of the prepared silica coated Cu nanoparticles. Our results also demonstrated that concentration of CTAB showed significant affect on the deposition of silica on Cu nanoparticles. The Cu@SiO₂ core-shell nanoparticles with Cu nanoparticles aggregated at the center was observed in this study perhaps due to the lack of adjustment of the concentrations of the water, catalyst and precursors. Further study is needed to optimize the preparation conditions to control the core-shell structure, shape and size. Work toward this direction is also in progress. Additionally, MW method is an excellent green process for its short reaction time and can be applied to synthesize a large variety of silica coated colloidal nanoparticles such as Pt, Co, CdSe, and so forth.

Fig.6 XPS survey scan spectra of uncoated Cu nanoparticles (a) and silica coated Cu nanoparticles prepared by MW technique (b).

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