Ultra-small Bismuth Particle in Dendrimer Protected by Polyvinylpyrrolidone

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Ultra-small metal particles are attractive materials exhibiting unique physical and chemical properties. In this study, we have produced polymer composites of 1-nm sized bismuth particles using phenylazomethine dendrimer templates and linear polymers. The formation of the polymer film with bismuth particles was revealed by STEM measurements. The stability of the ultra-small bismuth particles was demonstrated by XPS measurements. Variations of the protecting polymers were also successfully obtained by using polystyrene and polythiophene.

Keywords: Dendrimer, Bismuth, 1-nm sized particle, Polyvinylpyrrolidone

1. Introduction

Metal-polymer composites are useful materials for inorganic particles, and various types and methods have been reported. In these cases, the reduction of metal salts with polymers is a major approach for their preparation. It enables control of the particle morphologies by the choice of the polymers type [1]. In addition, the polymer increases the stability of the particles, and provides the possibility for applications such as catalyses and optical/electrical devices [2-5]. Among the polymers, polyvinylpyrrolidone (PVP) is attractive due to its favorable solubility in various solvents, affinity to various polymers and film formation properties.

In contrast, dendrimers [6-11] have been used for the fabrication of sub-nano sized particles based on the controlled coordination of the metal salts on the branches and the shell-effect for protection of the fabricated particles [12,13]. We have investigated the fabrication of precisely size-controlled sub-nano particles using the 4th generation dendritic polyphenylazomethines (DPAG4). The DPAG4 have a stepwise assembling ability for metal salts or other Lewis acidic units [13,14]. It enables the fabrication of size-regulated metal or metal oxide particles because the number of the assembled metal salts in the DPAs can be regulated. The fabricated platinum particles [15-21], gold particles [22-24] and aluminum clusters [25] showed unique properties including a high catalytic activity and superatomic nature. The size-controlled metal oxide particles were also synthesized by this dendrimer method. Sub-nano sized particles of titanium dioxide [26], tin oxide [27] and iron oxide [28] were reported, and they demonstrated a quantum sized effect and unique catalytic activity depending on their sizes. These research studies demonstrated the specific properties of sub-nano and 1-nm sized materials. The DPAG4 dendrimer plays a role for protection of the particle in it, however, it has a space such that the outer molecules have access to the particles. This space decreased the stability of the sub-nano sized particles.

We have now achieved metal-polymer composites with 1-nm sized metal particles in the DPAG4 by using PVP or other linear polymers to protect the particles. This method made the handling of the ultra-small particles easy. The protection was demonstrated using bismuth particles or clusters since they are expected to have optical properties in the visible and near infrared ranges [29,30]. Therefore, we developed a procedure for the controlled assembly of BiCl₃ in the DPAG4 [31] for
1-nm sized particles.

2. Experimental

2.1. Materials

BiCl$_3$ was purchased from Kojundo Chemical Laboratory Co., Ltd., and recrystallized from toluene before use. The recrystallization was conducted from acetonitrile and 1,4-dioxane in an Ar-filled glovebox. The amount of solvents with the crystal was determined by organic elemental analysis. Polyvinylpyrrolidone (PVP, average m.w. = $4 \times 10^4$), polystyrene (PS, average m.w. = $25 \times 10^4$) and polythiophene (PT) were obtained from Tokyo Chemical Industry Co., Ltd., Aldrich, and Wako Laboratory Chemicals, respectively. They were used without further purification. Dehydrated acetonitrile, dichloromethane, methanol and 1,4-dioxane were purchased from Kanto Chemical Co., Inc. The DPAG4 was synthesized according to a previously reported method [32].

2.2. Characterization

The UV–vis spectra were recorded at 20 °C using a Shimadzu UV-3100PC spectrometer with a quartz cell having an optical length of 1 cm. The XPS spectra were obtained by the Shimadzu ESCA-3400HSE. Mg $K\alpha$ (20 kV, 10 mA) radiation was used as the X-ray source. Polymer protected samples were sputtered by an Ar ion gun before the measurements. The spectra were standardized according to the C 1s peak (sp$^2$ carbon of HOPG) at 284 eV. The STEM images were obtained using a transmission electron microscope (JEOL, ARM-200F) by the HAADF method. The STEM samples were prepared on a microgrid with a Cu mesh (Okenshoji Co., Ltd. or Nisshin EM Co., Ltd.).

2.3. UV-vis titration of BiCl$_3$ versus DPAG4

DPAG4 and recrystallized BiCl$_3$ were dissolved in acetonitrile/dichloromethane (1/1) and acetonitrile solvents, respectively, in an Ar-filled glovebox. The specific amount of the prepared BiCl$_3$/acetonitrile (2.70 mM) solution was then added to the DPAG4 solution (3.31 µM), and the complexation reaction was monitored by UV-vis spectroscopy.

2.4. Fabrication of polymer protected bismuth particles in the DPAG4

Twelve equivalents of BiCl$_3$ in an acetonitrile solution were added to the DPAG4 solution (acetonitrile/dichloromethane = 1/1, 3.0 mL) in an Ar-filled glovebox. The assembled BiCl$_3$ units in the DPAG4 were then reduced using NaBH$_4$ in methanol (0.28 M, 5.0 µL). Each polymer (PVP, PS or PT) solution of dichloromethane (2 mg/mL, 2 mL) was added to the prepared solution of the bismuth particles under vigorous stirring.

3. Results and discussion

3.1. PVP protected bismuth particles in the DPAG4

One-nm sized bismuth particles were synthesized from a bismuth complex precursor, 12BiCl$_3$-DPAG4 (Fig. 1a). The 12BiCl$_3$-DPAG4 was prepared in a mixed solution of dichloromethane and acetonitrile, and the coordination was monitored by UV-vis absorption spectroscopy. The stepwise assembly of BiCl$_3$ into the DPAG4 was confirmed by the shift in the isosbestic point in the graph (Fig. 1b). The equivalent of each isosbestic point agreed with the number of imine parts in the layers of the DPAG4.

Reduction of the assembled BiCl$_3$ was conducted using NaBH$_4$, then a PVP solution was added to the solution of the bismuth particles in the DPAG4 (Fig. 2a). Scanning transmission electron microscope (STEM) observation showed size-controlled particles on the PVP polymer. The observed size was found to be about 1 nm (Figs. 2b-d). We also revealed that a good film form of the PVP polymer.

3.2. Stability of the PVP protected bismuth particles

The oxidation state of the fabricated bismuth particles was determined by X-ray photoelectron spectroscopy (XPS). The samples were drop-cast on
Fig. 2. PVP protection of the sub-nano sized bismuth particles in the DPAG4. (a) Procedure of the experiment. (b,c) Scanning transmission electron microscopy images. (d) A histogram of the observed diameters of the particles in STEM images.

HOPG and sputtered by an Ar ion gun before measurement. The observed binding energy of the Bi 4f5/2 suggests successful reduction to the metallic bismuth particles (Fig. 3a). The stability under ambient conditions was then revealed. The binding energy maintained the value for several hours. In contrast, the Bi 4f5/2 peak of a sample without PVP protection showed higher shift of the binding energy for 12 hours (Fig. 3b). The difference shows a certain advantage of the polymer protection for stabilization of the sub-nano sized metal particles in the dendrimer.

3.3. Variation of the polymers
The PS and PT polymers were used for expanding the variations that can protect the ultra-small particles in the DPAG4 without aggregation. Each sample was prepared using a dichloromethane solution of PS or PT for protection. The samples were dropcast on microgrids and were observed by STEM. Both samples showed size-controlled particles on the polymers (Fig. 4).

Fig. 3. X-ray photoelectron spectroscopy results of the PVP protected 1-nm sized bismuth particles. (a) An XPS spectrum of the as-prepared sample. The spectra was deconvoluted into three peaks corresponding to Bi 4f5/2, Bi 4f7/2 and Si 2s. (b) Time dependency of the binding energy of the Bi 4f5/2 peaks. Blue circles and orange squares are with and without PVP protection, respectively.

Fig. 4. STEM images of bismuth particles with DPAG4 on the polymers. The polymers are (a) polystyrene and (b) polythiophene.

4. Conclusion
Polymer protection of the 1-nm bismuth particles in the DPAG4 was successfully achieved using a PVP polymer. STEM measurements revealed the size of the particles on the PVP. XPS spectra of the Bi 4f5/2 peak revealed the reduced oxidation state in the as-prepared state, and the PVP played a significant role in protecting the ultra-small particles. The series of these findings are useful for expression of the properties that the ultra-small materials possess.

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