

Spectroscopic Investigation of Dendrimer-Encapsulated Gold Nanoclusters

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We have carried out the spectroscopic studies of dendrimer-encapsulated Au nanoclusters smaller than 2.4 nm. In this study, a 1.5th generation sodium carboxylate-terminated polyamidamine dendrimer was used as a template to control the size and stability of Au nanoclusters. The dendrimer-encapsulated Au nanoclusters were prepared by the chemical reduction of Au ions loaded within the dendrimer templates. The synthesized smallest nanocluster used in this work shows the strong blue photoluminescence at 2.8 eV photon energy, while larger nanocluster shows no photoluminescence. Furthermore, we carried out the X-ray photoemission study in the valence-band region of dendrimer-encapsulated Au nanocluster. From these results, we will discuss the size dependent properties of Au nanoclusters encapsulated within the dendrimer templates.

Key words: Au nanocluster, Polyamidamine dendrimer, Photoemission spectroscopy, Size effect

1. INTRODUCTION

Metallic nanoclusters containing tens to a hundreds atoms are attracted much attention, since they exhibit the characteristic optical and electronic properties due to the quantum confinement effects.¹⁻³ These properties are highly influenced with the nanocluster size. Thus, in order to observe the intrinsic size dependent phenomena, it is important to prepare the monodispersed nanoclusters. Recently, the nanoclusters encapsulated within the dendrimers have been chemically synthesized by several groups.⁴⁻⁸ Dendrimers are branched polymers with a layered and treelike structure, that have reactive end groups. In the case of metallic nanoclusters encapsulated within the dendrimer molecules, nanocluster size is determined by the size of the host dendrimer templates, thus, the uniform and very small nanocluster can be obtained. Furthermore, nanoclusters exhibit no aggregation due to stabilization by the dendrimer, and can be easily controlled their solubility by exchange the terminal of the dendrimer. These properties are very suitable to the future application such as drug delivery, biosensing, and catalysis.⁹⁻¹² In order to elucidate intriguing properties and to develop the future device, systematically characterization of their fundamental properties is important.

In this article, we prepared the Au nanoclusters encapsulated with the different size within 1.5th

generation sodium carboxylate- (G1.5-COONa-) terminated polyamidamine (PAMAM) dendrimers. We characterized the synthesized Au nanoclusters encapsulated within the G1.5-COONa-terminated PAMAM dendrimer with the photoluminescence and X-ray photoemission spectroscopies. From these results, we will discuss the size dependent properties of dendrimer-encapsulated Au nanoclusters.

2. EXPERIMENT

Dendrimer-encapsulated Au nanoclusters were prepared by one phase reaction at 0 °C. We used the G1.5-COONa-terminated PAMAM dendrimer as a template molecule. A 2.5 μmol of G1.5-COONa-terminated PAMAM dendrimer methanol solution was mixed with 10 ml of methanol solution containing the 250 μl of Au chloride (30 mM). In order to sequester Au ion into dendrimers, the solution was vigorously stirred for one hour. Then, equivalent sodium borohydride was added into the solution as a reduction agent with the stirring for 1 hour. In this process, the encapsulated Au ions were reduced within the dendrimer, and then, form the dendrimer-encapsulated Au nanocluster. The obtained nanocluster solution was dried with the rotary evaporator and redissolved into the water for the filtering treatment described below. The obtained nanocluster solution contains the large nanoparticles that would not

would not be encapsulated within the dendrimer. Therefore, the nanocluster solution was filtered several times with a centrifugation in order to remove the base and to improve the size distribution. Finally, we obtained two nanocluster samples with the different nanocluster sizes.

The size distribution in the diameter and shape of the present dendrimer-encapsulated Au nanoclusters were observed by the transmission electron microscope (TEM, V-7000, HITACHI). We performed the photoluminescence measurement with a spectrofluorometer (FP6600, JASCO) of dendrimer-encapsulated Au nanoclusters in aqueous solution. Moreover, we carried out the X-ray photoemission (XPS) measurement using the angle-integrated photoelectron spectrometer (CLAM2, VG Microtech) with $MgK\alpha$ line ($h\nu = 1253.6$ eV) as the excitation source. For the XPS measurements, the synthesized dendrimer-encapsulated Au nanoclusters aqueous solution are dried, and dissolved in the methanol. After that, these obtained nanoclusters were supported on the highly oriented pyrolytic graphite (HOPG) substrates by evaporating the solvent (methanol) from the solution of dendrimer-encapsulated Au nanoclusters on the single-crystalline HOPG cleaved surface in a nitrogen-filled glove bag directly connected to the ultrahigh-vacuum photoelectron spectrometer. Then the samples were transferred into the photoemission analysis chamber without exposure to air. All spectroscopic measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows the TEM micrograph and size distribution for the larger Au nanoclusters encapsulated within G1.5-COONa-terminated PAMAM dendrimer (referred as sample #1) used in this study. The size distribution was measured from the several TEM micrographs of the corresponding sample. The mean diameter and standard deviation of sample #1 are 2.4 nm and 0.4 nm, respectively. As shown in Fig. 1, the present dendrimer-encapsulated Au nanoclusters show the spherical shape, and each nanocluster separates from the neighboring nanoparticles, indicating that the present Au nanoclusters are well encapsulated within the dendrimer templates. However, since the diameter of dendrimer molecule is about 3 nm, Au nanoclusters larger than 3 nm in Fig. 1 are considered to be clusters that are not encapsulated within the PAMAM dendrimers. In addition, it is found that the number of Au nanoclusters is significantly high. This means that the present synthesis procedure has high efficiency for preparation of nanocluster. On the other hand, we could not observe the smaller nanocluster sample (referred as sample #2) used in this study by means of TEM, due to their smaller cluster size than the spatial resolution of TEM. Thus, the nanocluster size of sample #2 is considered to be 1-2 nm.

Figure 2 shows the photoluminescence spectra of the present synthesized samples #1 and #2 in aqueous

solution, measured at room temperature. Both photoluminescence spectra are measured with excitation photon energy of 3.7 eV. As shown in Fig. 2, it is found that the sample #1 shows no photoluminescence, but the sample #2 shows the strong visible photoluminescence centered at approximately 2.8 eV photon energy. The origin of the present photoluminescence of sample #2 is likely to be the photoluminescence from the PAMAM dendrimer. However, sample #1 that also contains the dendrimer molecule shows no distinct photoluminescence, thus the contribution from the dendrimer molecules to the photoluminescence spectrum is considered to be negligible. Therefore, the photoluminescence from the sample #2 is attributed to that from the Au nanocluster. Their photoluminescence of the smaller nanocluster with diameter of 1-2 nm might be new visible optical transition that results from the change of electronic structure due to size effect.

Figure 3 shows the XPS spectra of present synthesized dendrimer-encapsulated Au nanoclusters (samples #1 and #2) on the HOPG substrates at room temperature measured with the $MgK\alpha$ line ($h\nu = 1253.6$ eV). In Fig. 3 the photoemission spectra observed for bulk Au polycrystalline is also shown for a comparison.

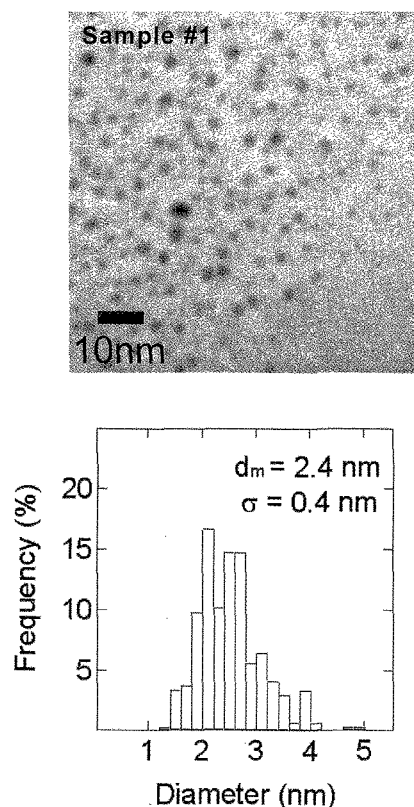


Fig. 1. TEM micrograph and size distribution of Au nanoclusters encapsulated within G1.5-COONa-terminated PAMAM dendrimer (referred as sample #1). The mean diameter d_m and standard deviation σ are 2.4 nm and 0.4 nm, respectively.

The valence band photoemission spectrum of bulk Au crystalline in Fig. 3 is identical with the previously reported ones.¹³ The broad feature around 3-8 eV binding energy is derived from primary Au 5*d* states. These Au 5*d*-derived features dominate the valence-band XPS spectra, because of their higher cross section than the *sp* electronic states of Au, C, and O (involved in HOPG substrate and G1.5-COONa-terminated PAMAM dendrimer) in the relevant exciting energies. Therefore, we will discuss the nanocluster diameter dependence of Au 5*d*-derived valence band. As shown in Fig. 3, the Au 5*d*-derived features of the bulk Au crystalline and sample #1 display the well-defined *d*-band doublets. However, it is found that the apparent spin-orbit splitting of sample #1 is narrower than bulk crystalline. On the other hand, it is found that the *d*-band doublet in the XPS spectrum of sample #2 is not clearly observed. Previously, Tanaka and Takeda have reported the similar decreases of the apparent spin-orbit splitting in the valence-band XPS spectra with decreasing the size of dodecanthiolate-passivated Ag nanoparticles in the size range of 3.5-5.2 nm.¹⁴ They have concluded that this decrease of apparent spin-orbit splitting with decreasing the nanoparticle diameter originates from the increasing the contribution from surface atoms as described below. It has been well established that the noble metal *d-d* interaction in bulk crystallite is very strong and the Au 5*d* band width and apparent spin-orbit splitting decrease with the decreasing of the

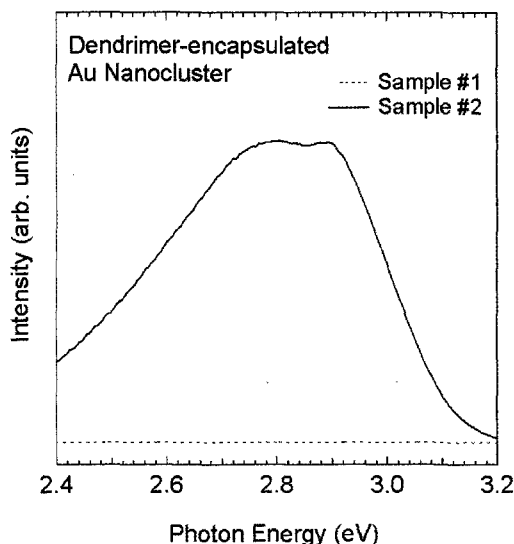


Fig. 2. Photoluminescence spectra of Au nanocluster encapsulated within G1.5-COONa-terminated PAMAM dendrimer in aqueous solution, measured at room temperature. Photoluminescence spectra are measured with excitation photon energy of 3.7 eV. Dashed and solid lines correspond to the sample #1 and #2 (see text), respectively.

coordination number of the nearest atom.¹⁵ In fact, it has been reported that the adsorption of metal atoms on the metallic substrate¹⁵ and alloying¹⁶ induce the reduction of this direct interaction and this will induce the reduction of this direct interaction and this will reduce the intrinsic noble-metal *d*-derived band width and the associated spin-orbit splitting effects. The apparent spin-orbit splitting can be expressed as,

$$\Delta_{5d} = (\Delta_{\text{band}}^2 + \Delta_{\text{s.o.}}^2)^{1/2}$$

where Δ_{band} is the band broadening contribution and $\Delta_{\text{s.o.}}$ is the true atomic spin-orbit splitting. The band broadening contribution Δ_{band} decreases with the number of nearest neighbors. The surface atoms have the smaller number of the nearest neighbor than the atom in bulk. Therefore, the surface *d*-derived band and the associated apparent spin-orbit splitting are narrower than the corresponding bulk. In the nanocluster systems, the surface atom ratio increases with decreasing the nanocluster size. Therefore, the band broadening contribution Δ_{band} decreases with decreasing the nanocluster size. Thus, the apparent spin-orbit splitting becomes smaller with the decreasing with the

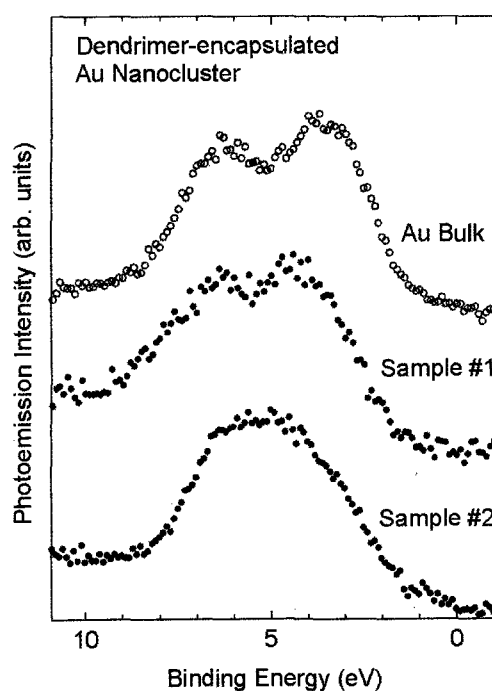


Fig. 3. Valence-band X-ray photoemission spectra of Au nanocluster encapsulated within the G1.5-COONa-terminated PAMAM dendrimer supported on the HOPG substrates measured with MgK α line ($h\nu = 1253.6$ eV) at room temperature. The top spectrum shows the valence-band photoemission spectra observed for bulk Au polycrystalline.

nanocluster size. This explains why the apparent spin-orbit splitting of dendrimer-encapsulated Au nanocluster with mean diameter of 2.4 nm (sample #1) becomes narrower than the Au bulk crystalline. The apparent spin-orbit splitting of sample #2 is expected to be smaller than sample #1. Therefore, the *5d*-derived feature in the valence band XPS spectrum of sample #2 reflects the narrowed apparent spin-orbit splitting as a result of reducing the nanocluster size. As described above, the nanocluster size of sample #2 is smaller than 2nm. For instance, in the case of the nanocluster with the diameter of 2 nm, it is estimated that 70 % of atoms are coordinated at their surface. Thus, it is considered that the surface atom derived electronic structure reflects the valence band XPS spectrum.

In order to elucidate the detailed features of photoluminescence from dendrimer-encapsulated Au nanoclusters, the information of their electronic structures are important. Therefore, we have carried out the photoemission study of the present fluorescent Au nanocluster. In addition, it has been reported that the extremely small nanocluster has the discrete electronic structure,⁷ though we could not observe such molecule-like electronic structure due to the present XPS measurements. For the more detailed discussion about the photoluminescence and the discrete electronic structures of Au nanocluster, we have to elucidate the occupied and unoccupied electronic structures in the vicinity of Fermi-level by the high-resolution core-level absorption with synchrotron radiation, photoemission and inverse-photoemission spectroscopies.

4. CONCLUSION

We have synthesized G1.5-COONa-terminated PAMAM dendrimer-encapsulated Au nanocluster with different sizes, and have characterized their optical properties and electronic structure. From the photoluminescence measurement, it is found that the smaller nanocluster used in this work (sample #2) shows the strong blue photoluminescence around 2.8 eV photon energy. From XPS photoemission measurement in the valence-band region, it is found that the apparent spin-orbit splitting of Au *5d*-derived band decreases with decreasing the nanocluster size. This is attributed to the increasing of the relative number of surface to inner atoms.

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