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Chiral Glutathione-protected Ag Triangular Nanoplates Synthesized by Protectant-substitution Reaction: Chiroptical and Surface Structure Analysis

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Chiral Ag:SG (glutathione) triangular nanoplates were synthesized by substitution reaction of achiral Ag:poly(vinylpyrrolidone) (PVP) nanoplates with glutathione free GSH molecules. Analysis of the chiroptical properties of the synthesized nanoplates using a circular dichroism spectrometer revealed characteristic Cotton effects with wavelengths that corresponded well to those of plasmon resonances for Ag nanoplates. X-ray photoelectron spectrometry analysis of their chemical compositions revealed that complete substitution of PVP molecules with GSH molecules proceeds on the nanoplates.

Ag triangular nanoplates have attracted much attention owing to their unique geometric structures and optical properties, which indicate that they have the potential for use in various applications.[1] These unique points are known to be complementary to each other since their optical properties are induced by surface plasmon resonances (SPR) that originate from their structure.[1–3] In other words, there is a potential to tune the optical properties of nanoplates by changing their structure. In fact, recent studies have revealed that the color of the Ag nanoplate solution can be controlled by truncation.[2,3]

Chirality of nanomaterials has also attracted much attention because chirality signals are usually observed in most biological systems.[4–9] Recently, such chirality signals have been observed in metal nanomaterial systems. Whetten et al. observed chirality signals for small Au nanoparticles protected by chiral thiol molecules.[5] In this case, the signals appeared in a visible range completely different from chiral thiol molecules themselves. Additionally, these signals were found to depend strongly on the size of nanoparticles.[4,10,11] Tang et al. revealed that the shape of nanomaterials is important for the appearance of chirality signals.[12] They synthesized Au nanorods with a variety of aspect ratio and observed shape-dependent chirality signals. In spite of these extensive studies, fundamental origin of the chiroptical activity is still unclear, and it is desired to explore for other nanomaterial systems.

In this study, we examined synthesis of chiral Ag:SG triangular nanoplates from achiral Ag:poly(vinylpyrrolidone) (PVP) nanoplates where SG represents glutahione by substitution reaction. The Ag:PVP nanoplates were prepared by photoirradiation of ethanolic $AgNO_3$ solution with PVP molecules.[13,14] The chiroptical properties were analyzed by circular dichroism (CD) spectroscopy, while the structures, optical properties, and surface-coating structures of the products were analyzed by scanning transmission electron microscopy (STEM), absorption spectroscopy, and X-ray photoelectron spectroscopy (XPS), respectively. Additionally, their chiroptical property was compared with that for Ag:SG spherical nanoparticles.

Ag:PVP triangular nanoplates were prepared using a previously reported method.[13] In brief, $AgNO_3$ powder (3.5 mg, Wako Pure Chemicals) and PVP (0.8 g, $k = 30$, $M_w = 40000$, Tokyo Kasei) were dissolved in ethanol. The Ag:PVP nanoplates were synthesized by irradiation of the mixed solution by a high-pressure Hg lamp (USH-500SC, Ushio) equipped with a wavelength selective mirror (UV365, Ushio) for 42 h at room temperature. Subsequently, the Ag:PVP solution (3.0 mL) was mixed with aqueous glutathione solution (2 μmol, GSH, Wako Pure Chemicals) and stirred at room temperature under an inert atmosphere. After overnight stirring, the obtained precipitates were purified for several times by the following process in order to remove released PVP and excess GSH molecules; the precipitates were collected by centrifugation, washed by ethanol, and redispersed with ethanol. On the other hand, Ag:SG spherical nanoparticles were basically synthesized by the same method except for the irradiation time of 3 h instead of 42 h.[14]

The as-prepared solution was filled in a rectangular quartz cuvette with an optical length of 1 cm. CD spectra were recorded with a JASCO J-820 spectropolarimeter. Absorption spectra for the solution were recorded using a JASCO V-530 spectrophotometer. Meanwhile, bright-field STEM images of synthesized colloids deposited of the as-prepared solution onto collodion-coated copper grids were observed by field-emission SEM (S-5500, Hitachi High-Technologies) operated at 30 kV. The XPS spectra of colloids deposited onto Si substrate were measured using an X-ray photoelectron spectrometer (Kratos Analytical AXIS-His) with monochromatic X-ray Al Kα radiation (1486.6 eV). The binding energies were corrected using the Si 2p peak (99.6 eV) that originated from the substrate.[15]

As shown in Figure 1a, a sharp peak at 330 nm and a broad distribution above 500 nm (red solid line) were observed in

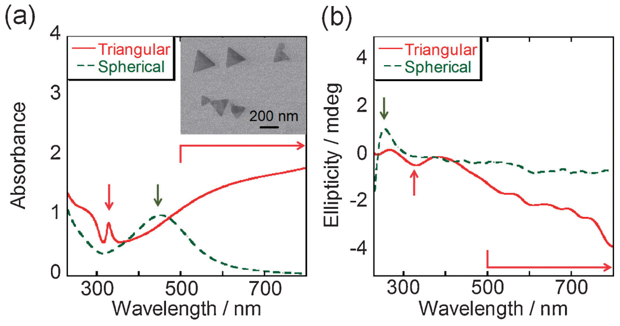

Figure 1. (a) Absorption spectra for Ag:SG triangular nanoplates (red solid line) and Ag:SG spherical nanoparticles (green dotted line). (b) CD spectra for Ag:SG triangular nanoplates (red solid line) and Ag:SG spherical nanoparticles (green dotted line).

optical absorption spectrum for nanoplates, while a single peak at 420 nm (green dotted line) was observed for nanoparticles. The observed features for nanoplates are known to agree well with those for typical triangular nanoplates which are ascribed to characteristic SPR of nanoplates;[1,2,13] therefore, the shape of nanoplates is not affected by the present substitution process. This is also confirmed by STEM image shown in the inset of Figure 1a. On the other hand, the observed 420-nm peak for nanoparticles agrees well with that for typical spherical nanoparticles.[14]

As shown in Figure 1b, the CD spectra for nanoplates (red solid line) exhibits three characteristic Cotton effects as a positive peak at 270 nm, a negative peak at 330 nm, and a negative distribution above 500 nm, while that for nanoparticles (green dotted line) exhibits one Cotton effect as a positive peak at 260 nm. The observed positive peak for both cases suggests that GSH molecules are chemically bound to the Ag surface of representative nanomaterials because it is known that a positive peak appears in this wavelength region for GSH molecules bound to metal nanoparticles while a negative peak appears for GSH molecules themselves.[16,17] Meanwhile, the wavelength for the observed negative peak and distribution are completely different from those for the GSH molecules but are similar to those for the characteristic SPR of nanoplates shown in the optical spectrum (Figure 1a). It is worthy to note that Ag:PVP nanoplates prior to GSH addition exhibit no signals (Figure S1[23]). These findings clearly indicate that new chiroptical properties were induced by the adsorption of chiral molecules in the achiral nanoplates. In other words, chiral electromagnetic currents are generated inside the metal nanoplates by the presence of GSH molecules as chiral chromophores.[9,11,18]

In the Ag 3d spectrum of nanoplates shown in Figure 2a, two peaks are observed at 368.1 and 374.1 eV. The lower peak is ascribed to metallic Ag $3d_{5/2}$ (368.1 eV),[19] and the energy difference between these peaks corresponds to a spin–orbit separation of 6 eV between Ag $3d_{3/2}$ and Ag $3d_{5/2}$. It is worthy to be noted that the observed binding energies are different from those for Ag:PVP nanoplates prior to GSH addition (367.5 eV).[13] In fact, the contribution of the Ag:PVP nanoplates for the observed peak was estimated as less than 1% (Figure S3[23]) when both peaks were assumed for curve-fitting analysis. These findings indicate that the PVP molecules are almost completely eliminated from the surface of nanoplates by the reaction.

In the S 2p spectrum shown in Figure 2b, a broad peak is present at 162.1 eV. Based on the spin–orbit separation of 1.2 eV between S $2p_{3/2}$ and S $2p_{1/2}$, this peak is deconvoluted into two components at 162.0 and 163.2 eV, which are exhibited as dotted lines. This lower binding energy is ascribed to the S–Ag bond (162.1 eV).[20] This agreement indicates that the GSH molecules are chemically adsorbed onto the surface of the nanoplates by the reaction.

In the N 1s spectrum shown in Figure 2c, a peak is present at 400.5 eV. Since two components are known to be present at 400.2 and 401.5 eV for the NH or NH_2 and NH^{3+} groups in the GSH molecules,[21] we deconvoluted this peak into these two components shown in Figure 2c as dotted lines. The good reproduction of the peak profile suggests that surface of the synthesized nanoplates is covered by GSH molecules. Additionally, although we also estimated the contribution of PVP molecules for this peak (399.3 eV),[13] we found that the contribution is less than ca. 2% (Figure S3[23]). These results suggest that protectant molecules of Ag nanoplates are largely substituted by GSH molecules. Furthermore, stoichiometry normalized by the number of N atoms was estimated to be $C_{20.1}N_3O_{6.6}S_{1.0}$ from the area ratio of the XPS spectra. The relative ratio of N, O, and S atoms is consistent with the stoichiometry of the GSH molecule as $C_{10}H_{17}N_3O_6S$, although the relative ratio of carbon was overestimated due to carbonaceous contamination on the surface which originates from adsorption/reaction of the various hydrocarbon species present in the atmosphere.[22]

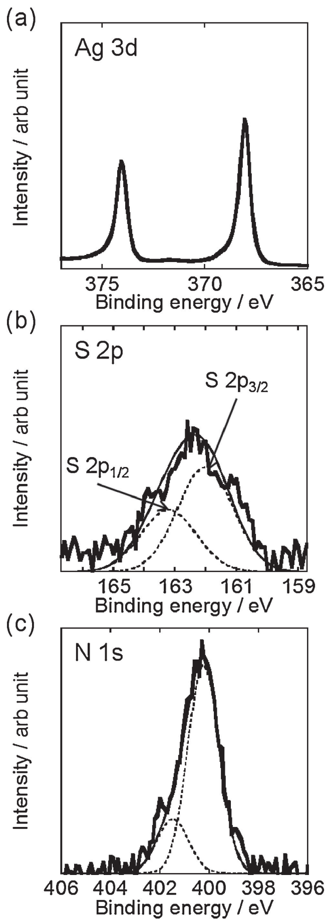

Figure 2. X-ray photoelectron spectra for Ag:SG nanoplates: (a) Ag 3d, (b) S 2p, and (c) N 1s spectra.

In conclusion, chiral Ag:SG triangular nanoplates were synthesized by protectant substitution reaction of achiral Ag:PVP nanoplates with GSH molecules. The obtained nanoplates showed characteristic Cotton effects in the CD spectrum which were induced by SPR of nanoplates. Chemical shifts of the binding energy observed upon XPS analysis revealed that GSH molecules attached to Ag nanoplates in the S–Ag bond and that PVP of Ag nanoplates is largely removed through substitution reactions with GSH.

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