Electronic Supplementary Information (ESI) for *PCCP*

Size dependence of magneto-optical activity in silver nanoparticles with dimensions between 10 and 60 nm studied by MCD spectroscopy

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MCD responses normalized to the concentration of nanoparticles and those normalized to the net volume of silver.

In metal nanoparticles, the sum of absorption and scattering components (or cross sections) represents the extinction of light, that is, extinction cross section. For Ag nanospheres, it is known that extinction cross section can be calculated using the formula;[1]

$$\text{extinction} = 0.434\,\sigma_{ext}\, l\, n,$$

where σ_{ext} is the extinction cross section in cm^2, l is the path length in cm, and n is the particle concentration in cm^{-3}. The relationship between σ_{ext} and mean particle diameter (D; $D \geq 29$ nm) has been well examined by Chumanov and co-workers,[1] so we could estimate the particle concentrations for samples **NP-3~NP-6** using this relationship. On the other hand, for nanoparticles small compared to the wavelength of the light, the dipole-based σ_{ext} is known to be proportional to the particle volume from the Mie theory,[2,3] so we could calculate the particle concentration for samples **NP-1** and **NP-2** using the relationship by assuming that spherical particles with the diameter of D are contained in each sample. Hence the particle concentrations obtained were 1.4×10^{-10}, 1.5×10^{-11}, 1.1×10^{-11}, 4.4×10^{-12}, 1.9×10^{-12}, and 8.1×10^{-13} (in cm^{-3}) for **NP-1** to **NP-6**, respectively. Then the MCD spectra normalized to the concentration of particles are shown in Fig. S1a. As a matter of course, the MCD signals normalized to the particle concentration became stronger when the size of the nanoparticles was larger.

Next, the net volume of Ag was calculated for each sample by assuming that the sample contains intact spherical particles with their mean diameter. Then the MCD responses are normalized to the net volume of Ag. The result is shown Fig. S1b. Interestingly, the decrease trend in normalized MCD responses as a function of size is quite similar to that obtained on the basis of the data normalized to the LSPR absorbance (Fig. 4 in the main text).

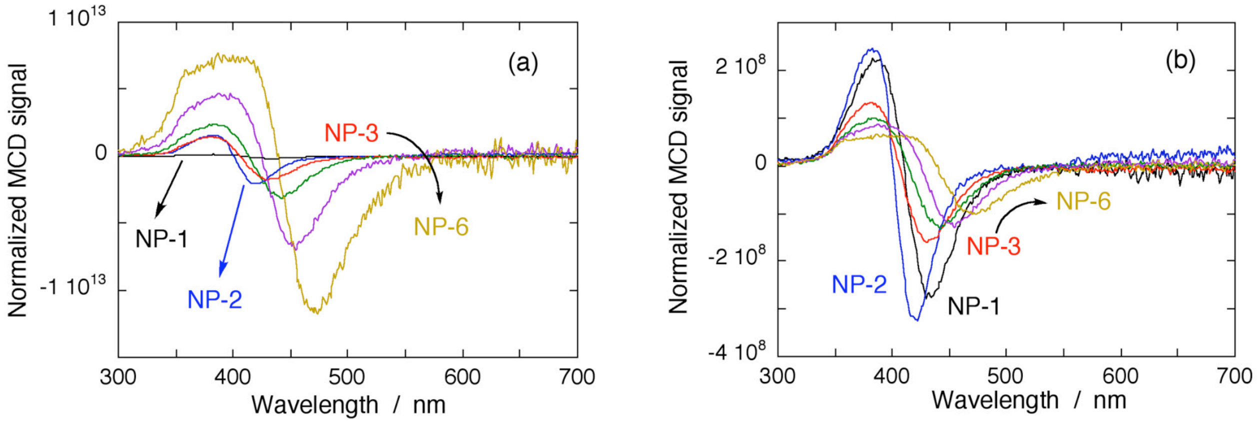

Fig. S1. MCD responses of the Ag nanoparticle samples (a) normalized to the concentration of particles, and (b) normalized to the net volume of Ag.

Electron micrograph, extinction, and A_p-normalized MCD spectra of TA-modified Ag nanoparticles with the mean diameter of 29.0 ± 2.3 nm.

We also prepared pure-TA-modified Ag nanospheres with the mean diameter of 29.0 nm. The particle size was controlled by changing the pH of the reaction solution. The TEM image, extinction and A_p-normalized MCD spectra of the sample are shown in Fig. S2. In the figures, we also compare the data of the present sample with those of **NP-3**, which has a similar mean particle diameter. The MCD spectra of these two samples are quite similar between them. Meanwhile, the LSPR linewidth for the TA-modified Ag nanoparticle sample (4540 cm^{-1}) was slightly narrower than that of **NP-3**, so a precise comparison of their MCD signals may be difficult. With a closer inspection, however, the MCD amplitude in the high-energy region for TA-modified Ag nanoparticle sample was slightly smaller than that for **NP-3**, implying that the ligand differences could more or less influence to the MO activity.

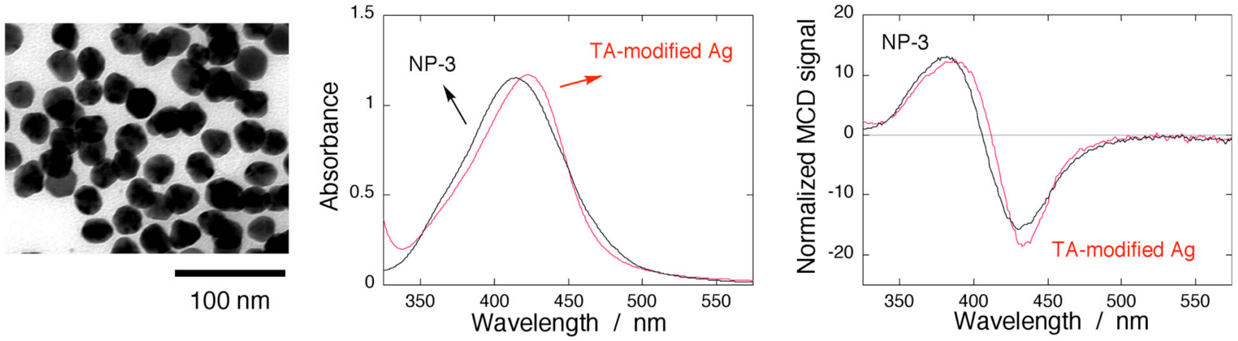

Fig. S2. TEM image, extinction, and A_p-normalized MCD spectra (+1.6 T) of TA-modified Ag nanoparticles. The average diameter of the sample was 29.0 ± 2.3 nm from the TEM image.

References

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