Supplementary information to Spray-drying-based surface-enhanced Raman spectroscopy: Effect of the silver nanoparticle aggregate size on the enhancement of Raman scattering

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Text S1. The average droplet diameter

The number concentration of the colloidal suspension of AgNPs (N_{AgNPs}) 0.01 wt% is 4.3×10^{11} mL^{-1}. At this concentration, it is assumed that it is dispersed in the droplet and 1 AgNP is present per droplet. The number of particles in the droplet (n) can be represented by Eq (S1) using the droplet diameter (D_{d}) and the number concentration of the colloidal suspension (N_{AgNPs}).

$$n = \frac{\pi D_{\mathrm{d}}^3}{6} \times N_{\mathrm{AgNPs}} \tag{S1}$$

The average droplet diameter can be calculated by calculating D_{d} at which $n = 1$.

Text S2. Primary particle size of AgNPs

Figure S1 exhibits the SEM image obtained by dropping the AgNPs colloid suspension on a copper plate and then drying it. The average primary particle size was measured to be 30 nm.

Text S3. Bouncing of particles may redistribute the size distributions of AgNPs deposited on the substrate.

Here we consider the difference in particle size distribution between SEM and SMPS from the Stokes number.

Function $C_{\mathrm{c}}(d_{\mathrm{s}})$, for Cunningham coefficient for Stokes diameter d_{s}

Stokes number of the impactor is expressed as

$$Stk = \frac{C_{\mathrm{c}}(d_{\mathrm{s}})\rho_{\mathrm{P}} d_{\mathrm{s}}^2 U}{9\mu W} \tag{S2}$$

where ρ_{P} is the AgNPs density, U is the average flow velocity at the nozzle, μ is the gas viscosity, W is the nozzle diameter. Stokes number of 48, 86 and 218nm AgNPs are 3.18, 5.74 and 14.8. The collection efficiency is almost 100% for any particle size, and they can be collected on the substrate. However, these Stokes numbers are much larger than the Stokes values at a collection efficiency of 50%, and the probability that particles colliding with the substance will bounce back without being collected. The velocity of particles (U_{i}) when they collide with the collision plate is estimated from the empirical

formula of rebound of particles[1].

$$\frac{U_{\mathrm{i}}}{U} = 1 - \frac{1}{4Stk} + \frac{1}{96Stk^2} \tag{S3}$$

The conditions under which particle rebound is predicted are as follows.

$$U_{\mathrm{i}} d_{\mathrm{s}} \sqrt{\frac{\rho_{\mathrm{P}}}{\rho_0}} > \Gamma \times 10^{-6}\ m^2 \cdot s^{-1} \tag{S4}$$

where ρ_{P}/ρ_0 obtained by dividing the particle density [gcm^{-3}] and, Γ has values ranging from 2.5 to 9.2 depending on the material and size of particles, type of impactor, etc. As a general criterion for particle bounce in impactors, a value of 5 is chosen for Γ. Value on the left side of Eq (S4) of 48, 86 and 218 nm AgNPs are 1.41×10^{-5}, 2.62×10^{-5}, and 6.76×10^{-5}. Any of the particle sizes satisfies Eq (S4) and the particles are expected to rebound. It suggests that the bouncing of the particles altered the particle size distribution on the substrate and affects the difference from the SMPS distribution.

Text S4. The UV-Vis spectrum and the size distribution of AgNPs in the suspention

The UV-Vis spectrum of AgNP suspension shows an absorption peak at around 395 nm (Fig. S2). The peak corresponds to the localized surface plasmon resonance (SPR) of AgNPs[2] that initiates SERS. Figure S3 shows the size distribution of AgNPs in the suspension of 0.001 wt% measured by DLS analysis. The average size of AgNPs was found to be about 46 nm that is roughly consistent with the primary particle size of AgNP (30 nm) and the average size of AgNP aerosols (38 nm).

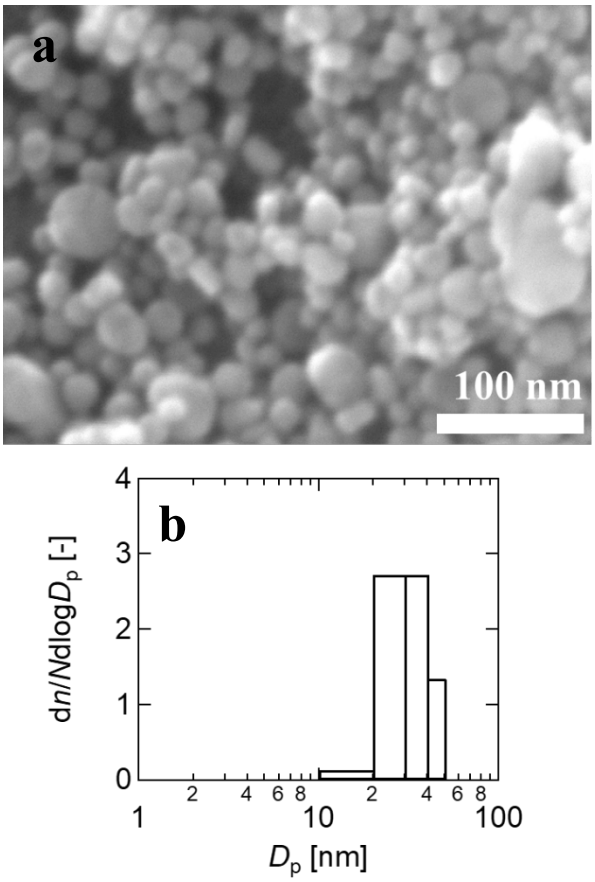

Figure S1. (a) SEM images and (b) size distributions of deposited AgNPs

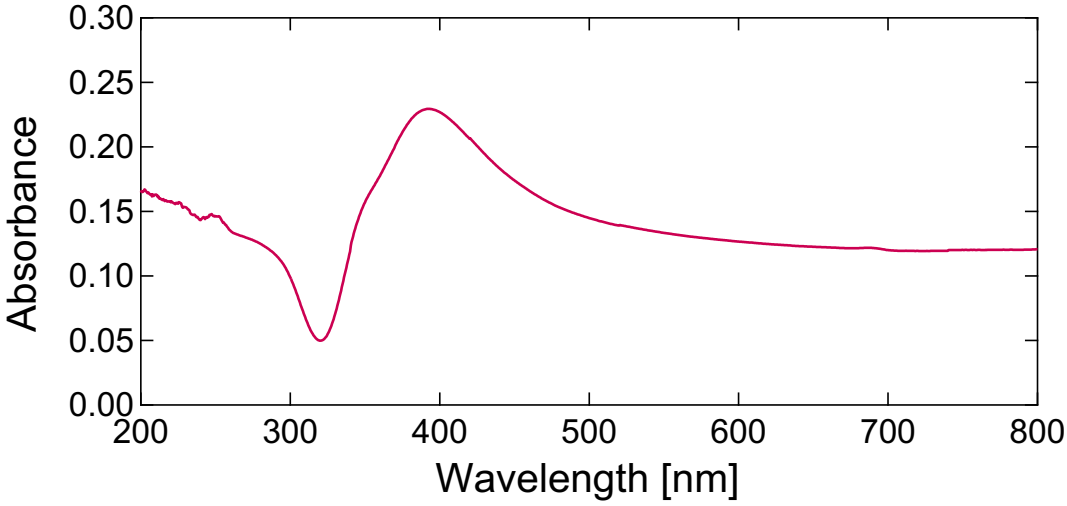

Figure S2. The UV-Vis spectrum of AgNP suspension

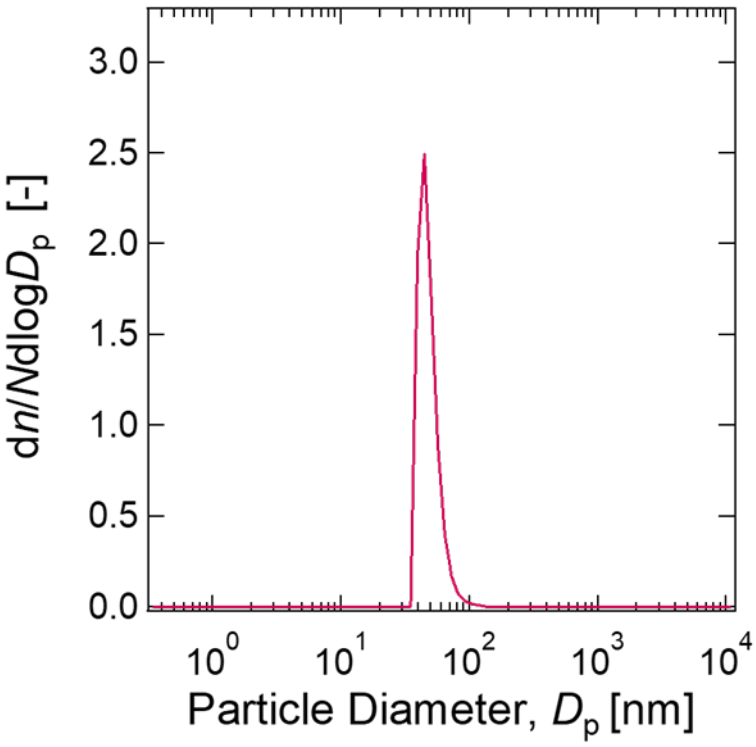

Figure S3. the size distribution of AgNPs in the suspension of 0.001 wt% measured by DLS analysis

References

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2. Dutra, M. A. L., Marques, N. do N., Fernandes, R. da S., de Souza Filho, M. de S. M. & Balaban, R. de C. ECO-FRIENDLY hybrid hydrogels for detection of phenolic RESIDUES in water using SERS. *Ecotoxicol. Environ. Saf.* **200**, 110771 (2020).