

Supporting Information for

Direct Chemical Synthesis of Plasmonic Black Colloidal Gold Superparticles with Broadband Absorption Properties

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Experimental Section

Synthesis of Au SPs

In a typical synthesis, 50 μmol of chloroauric acid (HAuCl_4 , Alfa-Aesar) was dissolved in 2 mL of ethylene glycol (EG, Samchun chemical Co., Korea). The solution was then added to 8 mL of oleylamine (OAm, Thermo Fisher Scientific Inc.) in a 24-mL vial at room temperature. The vial was kept at 150 $^{\circ}\text{C}$ in oil bath for 30 min until the color changed into completely black. The vial was taken out from the oil bath and cooled down to room temperature.

Preparation of Au SP film and optical measurements

The Au SP dispersion was 10 times concentrated and coated onto substrates by a spray coating method using an air brush (Monster BRUSH-001, Air Factory, Korea). Optical properties of Au SP film were measured using UV-vis-NIR spectrophotometer equipped with an integrating sphere under the UV-vis-NIR range (400 to 2500 nm). Total absorption of the sample was extracted as $A(\%) = 100 - T - R$ where A, T, and R are the total absorption, transmission, and reflection, respectively. For the laser beam reflection experiment, a water mist was spread by using an air brush to display laser beam pathway. A laser beam at a wavelength of 650 nm was directly incident on the Au SP and bulk Au films. The reflected beam was hit on a black screen.

Numerical calculation of UV-vis absorption spectra

Absorption spectra were numerically calculated by a commercial finite-difference time-domain (FDTD) solver (FDTD Solutions, Lumerical Inc.). The total-field-scattered-field source was applied to obtain absorption spectra and scattering cross sections of individual Au SPs. Perfectly matched layers were used on all boundaries of the numerical simulation domain to model infinite space. The number of the Au NPs in each SP is provided in Table S1.

Table S1. The number of Au NPs in each SP.

Black gold (each SP) size	# of Au NPs
210 nm	785
340 nm	4693
400 nm	7713
500 nm	14405

The minimum spacing between the nearest Au NPs was 2 nm to prevent overlapping of the Au NPs. Each Au NP was placed shell by shell from the center of the SP. On each shell, Au NPs were positioned by assigning their latitude and longitude on the shell. When positioning the NPs, the minimum spacing between NPs was set to 2 nm while a small randomness (smaller than the half of the minimum spacing) of the position was intentionally added to prevent a regular alignment of Au NPs to appear in any direction. The minimum mesh size was set to 0.4 nm, which is one-fifth of the smallest gap distance between Au NPs. The absorption cross-section

obtained from the simulations were used to find the total absorbance according to the Beer-Lambert law.

Preparation of SERS substrate

The Au SP dispersion was prepared in ethanol. The Au SP dispersion was drop-casted onto a quartz wafer (Shin-Etsu Chemical Co., Japan) and dried under ambient condition. A single-layer graphene on Cu foil (Graphene Research Center, Korea) was coated with poly(methyl methacrylate) (PMMA, Sigma Aldrich), and Cu was then etched by using ammonium persulfate (Sigma Aldrich) aqueous solution. Subsequently, the graphene-PMMA film was transferred onto the Au SP-quartz, and the PMMA layer was removed by using acetone. A single-layer graphene on single Au NP sample was prepared by using Au NP dispersion (Sigma Aldrich), and the same procedures were carried out.

Preparation for measurement of photothermal performance of the Au SPs

2 mL of PVP ($M_w = 10$ or 40 K, Sigma Aldrich) solution in ethanol (25 mg/mL) was added to 0.5 mL of as-synthesized Au SP dispersion in ethanol, and the mixture was stirred for 4 hr. Next, Au SPs were separated by centrifuging and washing with water. Finally, Au SPs were dispersed in 0.5 mL of water. 0.25 mL of Au SP dispersion (0.025 mmol Au) was taken in 48 well plate, and 980 nm laser at a power density of 0.2 mW/cm^2 was then irradiated for a certain period. The temperature was monitored by a temperature controller.

Calculation of photothermal conversion efficiency

The photothermal conversion efficiency (η) is defined by the following relationship.

$$\eta = \frac{hs(T_{max} - T_{surr}) - Q_{dis}}{I(1 - 10^{-A_{980}})} \quad (1)$$

where h is the heat transfer coefficient, s is the surface area of the container, and the value of hs is extracted from the Eq. 2 and Fig. S7.

$$hs = \frac{\sum m_i C_{p,i}}{\tau_s} \quad (2)$$

where m_i is the mass of component and $C_{p,i}$ is specific heat. A sample system time constant τ_s was calculated by applying the linear time data from the cooling period versus negative natural logarithm of driving force temperature as follows.

$$t = -\tau_s \ln(\theta) \quad (3)$$

In order to obtain the value of τ_s , a dimensionless parameter θ is introduced as follows.

$$\theta = \frac{T - T_{surr}}{T_{max} - T_{surr}} \quad (4)$$

As provided in Fig. S7a, the maximum steady-state temperature (T_{max}) of the dispersion was 38.1 °C and the surrounding temperature (T_{surr}) was 28.2 °C. Supplying the values of T_{max} and T_{surr} in Eq. (4), the value of τ_s is calculated to be 111 s by Eq. (3). In addition, $m_{ethanol}$, $m_{Au\ SPs}$, $C_{ethanol}$, and C_{gold} is 0.8 g, 0.008 g, 2.46 J/g·°C, and 0.129 J/g·°C, respectively. Then, the value of hs can be extracted to be 17.7 mW/°C. The heat dissipated from the light absorbed by the solvent and container (Q_{dis}) was independently measured to be 20 mW. The laser power (I) was 200 mW and the absorbance of the Au SPs at 980 nm (A_{980}) was 2.843.

Characterization

The size and shape of the Au SPs were analyzed by using a field effect-scanning electron microscope (JSM-6701F, JEOL, Japan). Transmission electron microscopy, scanning transmission electron microscopy, and high-resolution transmission electron microscopy images were obtained by using JEM-2100F (JEOL, Japan) microscope operated at an acceleration voltage of 200 keV. UV-vis spectra of colloidal Au SPs were recorded using a Hewlett-Packard 8453 UV-vis spectrometer. Total reflection, absorption, and transmission of the Au SP film were recorded by using a UV-vis-NIR spectrophotometer (Cary 5000, Agilent Technologies, USA) equipped with an integrating sphere accessory. Surface enhanced Raman scattering (SERS)

spectrum with an excitation wavelength of 532 nm was measured by using a SENTERRA Raman (Bruker). SERS spectrum with an excitation wavelength of 780 nm was measured by using a DXR Raman Microscope (Thermo Fisher Scientific). Heat generation from the Au SP dispersion was monitored by UP35A temperature controller (Yokogawa, Japan). The particle size distribution was measured by using a Zetasizer Nano ZS90 (Malvern Instruments, UK).

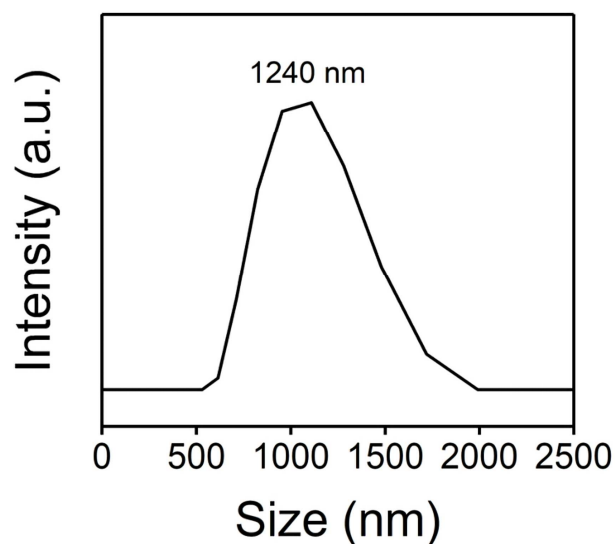


Figure S1. Particle size distribution of the Au SPs recorded by the dynamic light scattering measurement.

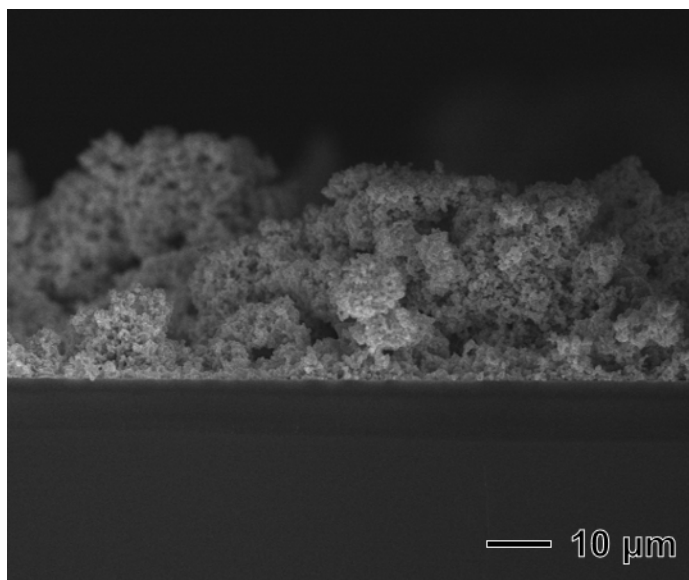


Figure S2. Cross-sectional SEM image of a Au SP film prepared by repeated spray coating of the Au SP dispersion in ethanol onto a quartz wafer.

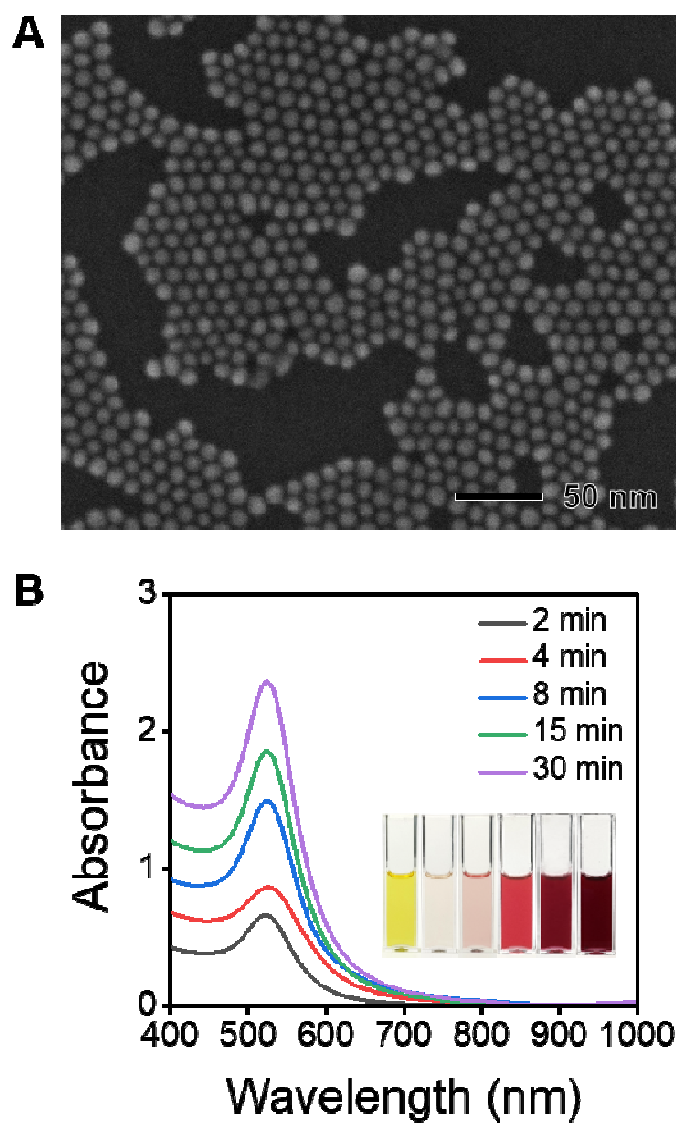


Figure S3. (A) SEM image of single Au NPs synthesized in the absence of EG and (B) UV-vis spectra recorded at different stages of the synthesis.

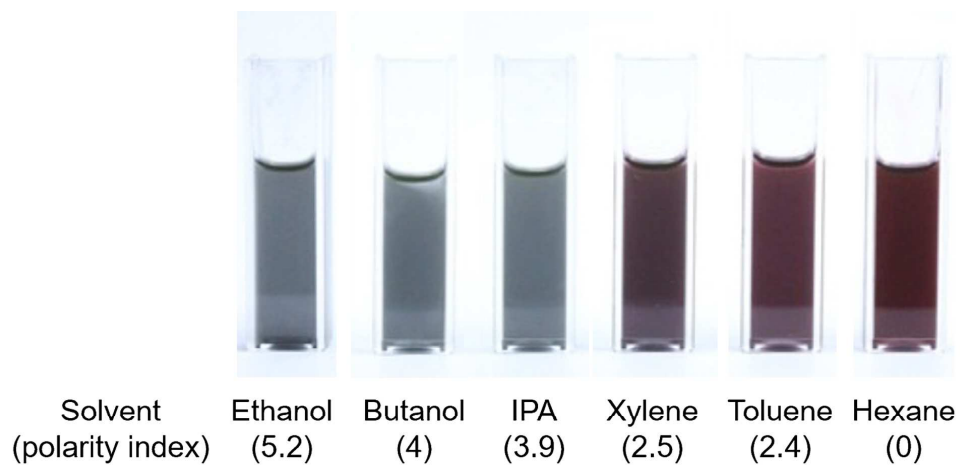


Figure S4. Photographs showing Au SPs dispersed in solvents with different polarities. In non-polar solvents such as xylene, toluene, and hexane, the SPs are disassembled into individual NPs.

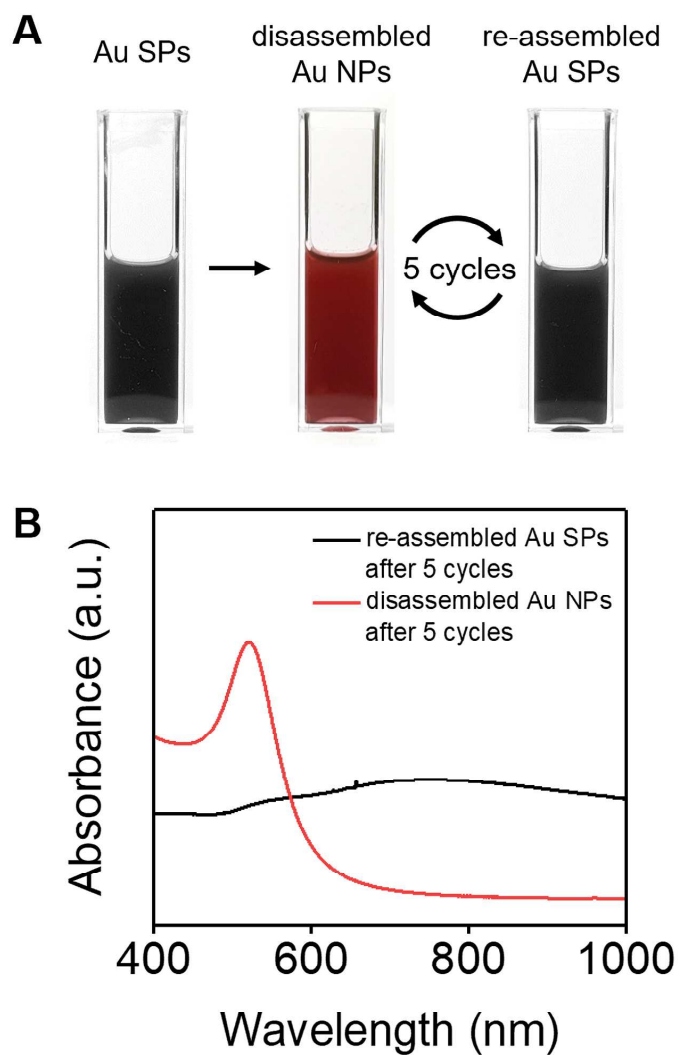


Figure S5. (A) Photographs showing the change in color of the Au SP dispersion during repeated cycles of the disassembly and re-assembly process. (B) UV-vis spectra recorded after 5 cycles of disassembly and re-assembly process.

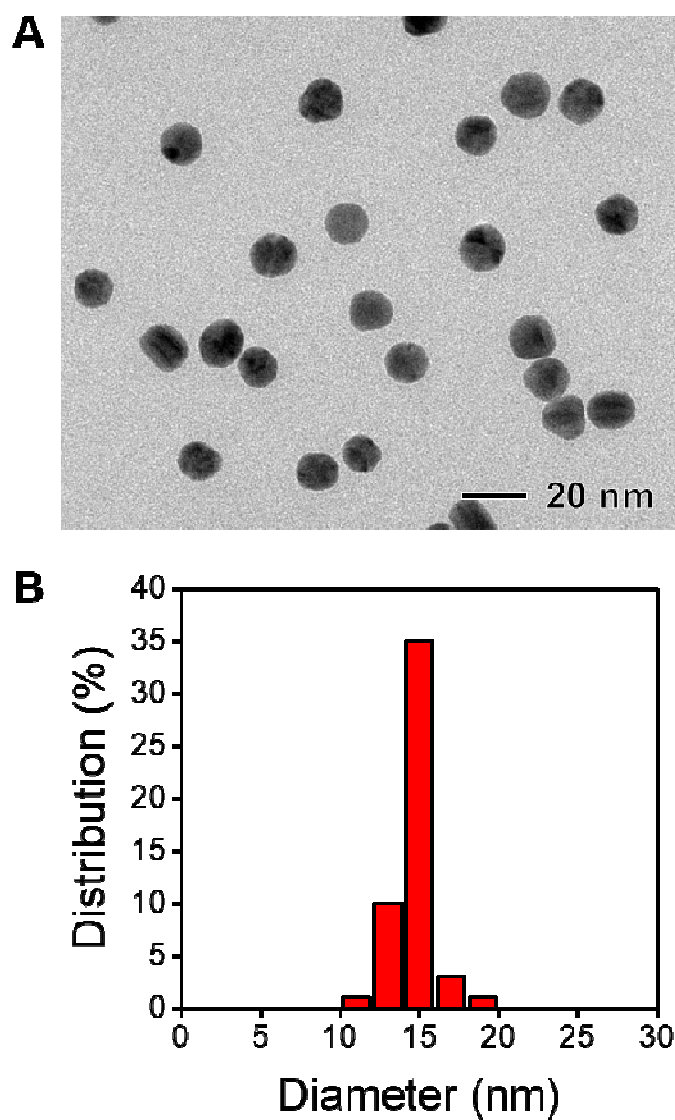


Figure S6. (A) TEM image and (B) particle size distribution of commercial Au NPs used in this study.

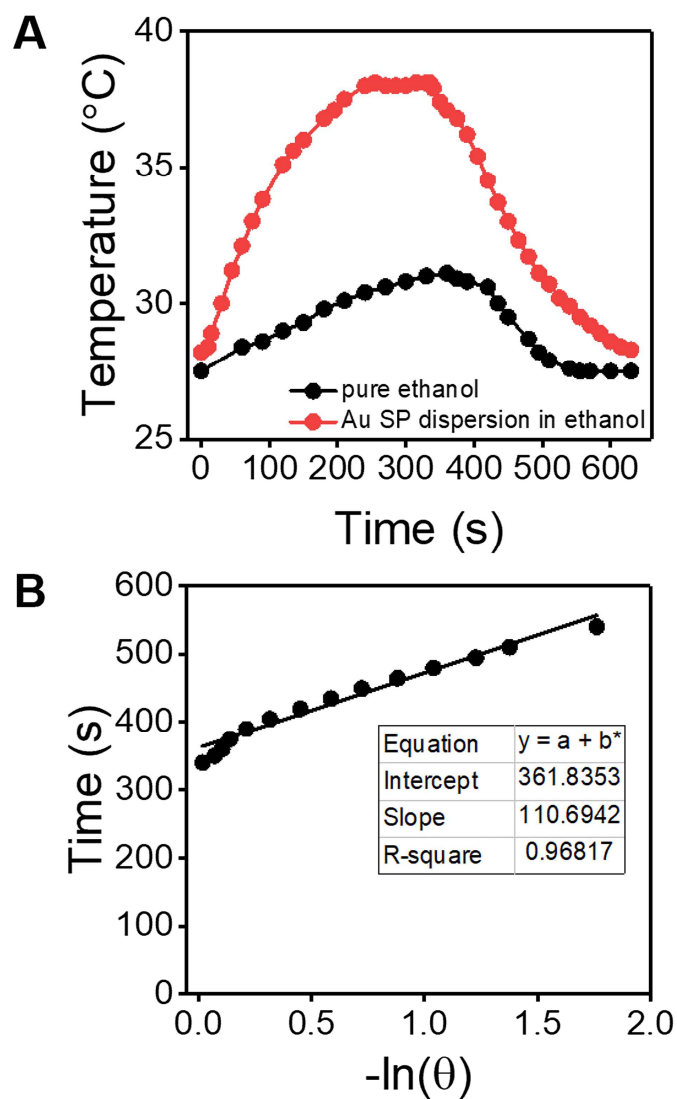


Figure S7. (A) Temperature profile of pure ethanol and Au SP dispersion in ethanol used for calculating the photothermal conversion efficiency of Au SPs. (B) The linear time data from the cooling period versus negative natural logarithm of driving force temperature of (A).

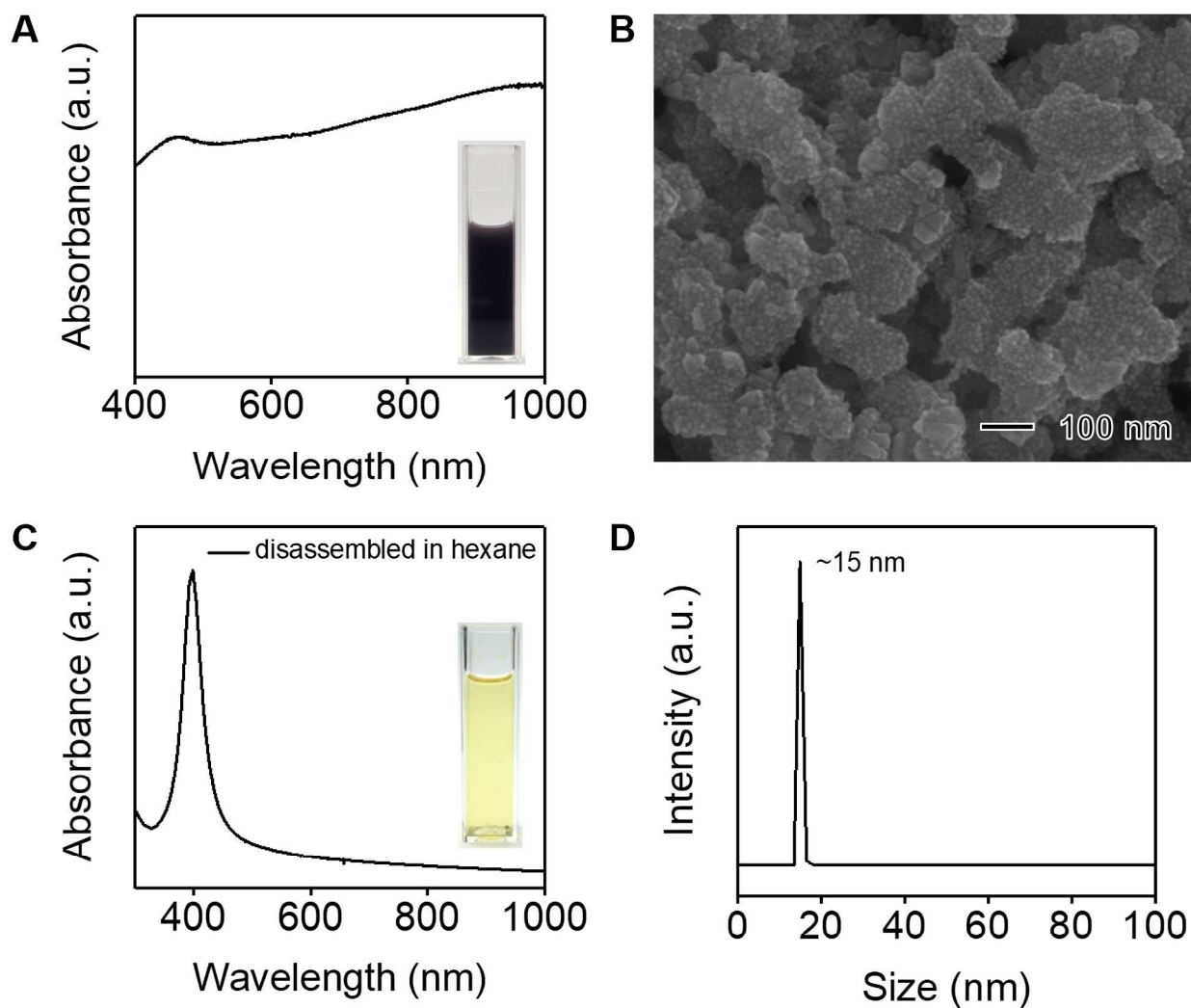


Figure S8. (A) UV-vis spectrum and (B) SEM image of colloidal Ag SPs. In (A), the inset shows a photograph of the as-prepared Ag SP dispersion. (C) UV-vis spectrum and (D) particle size distribution of the disassembled Ag NPs in hexane. In (C), the inset shows a photograph of the disassembled Ag NPs in hexane.

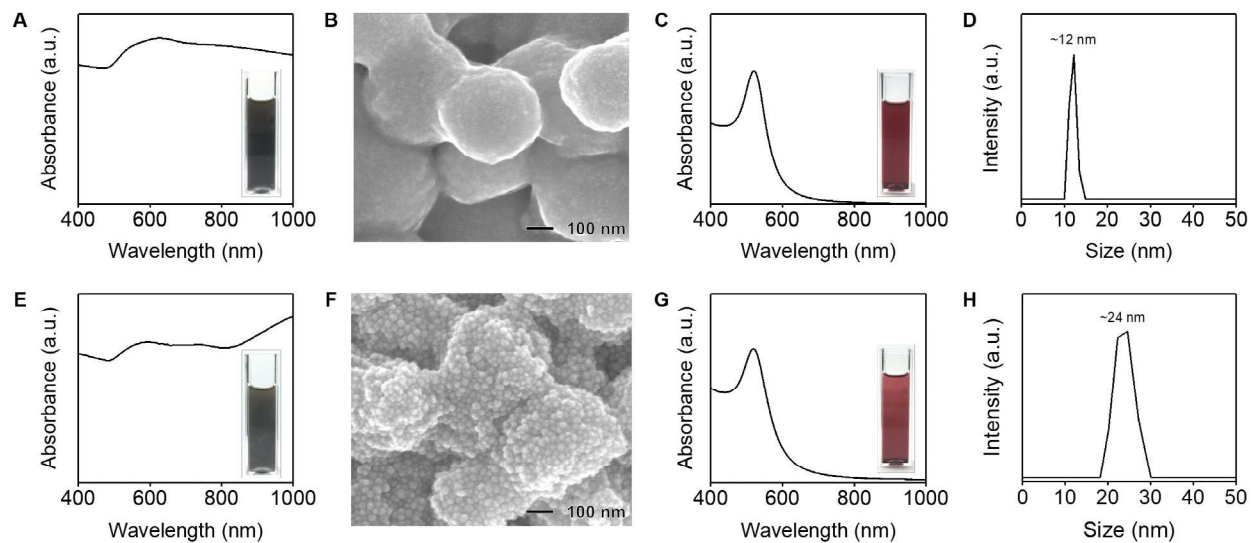


Figure S9. (A) UV-vis spectrum and (B) SEM image of Au SPs synthesized with hexadecylamine. (C) UV-vis spectrum and (D) particle size distribution of the disassembled Au NPs that had been prepared with hexadecylamine. (E) UV-vis spectrum and (F) SEM image of Au SPs synthesized with dodecylamine. (G) UV-vis spectrum and (H) particle size distribution of the disassembled Au NPs that had been prepared with dodecylamine.