Electronic Supplementary Information

for

Tuning Plasmonic Properties by Promoting the Inward Hg Diffusion *via* Oxygen Plasma Treatment in Gold Nanorods Coated with Mesoporous Silica Shell

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This document contains experimental methods and supplementary figures (Fig. S1 to S12).

Experimental Methods

Materials and Sample Preparation. Mercury (II) chloride ($HgCl_2$, ≥99.5%) and sodium borohydride ($NaBH_2$, ≥98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. The AuNRs@*m*SiO_2 used in this study were purchased from Nanopartz (Loveland, CO, USA). To prevent aggregation and maintain the proper concentration of the nanoparticles on the substrate surface, the colloidal solutions of AuNRs@*m*SiO_2 were diluted to the necessary concentration with 18.2-MΩ pure distilled water and sonicated for 15 min. The samples were made by spin-casting the diluted AuNRs@*m*SiO_2 solution onto a precleaned (ultrasonically in ethanol, distilled water, and isopropanol for 15 min, respectively) glass slide and allowed to dry. Afterward, the samples were exposed to Hg amalgamation and oxygen plasma treatment. For single-particle scattering microscopy and spectroscopy studies, a 22 × 22 mm no. 1.5 coverslip (Corning, NY) was placed on the glass slide. To investigate nanoparticles at a single-particle level and minimize the inter-particle LSPR coupling, the concentration of nanoparticles on the slide glass surface was controlled to be 1 μm^{-2} in this study.

Structural Characterization. A scanning electron microscope (SEM, JSM-6500F, JEOL, Japan) and a transmission electron microscope (TEM, JEL-2100F, JEOL, Japan) were used to characterize AuNRs@*m*SiO_2 before and after Hg amalgamation. The length and width of AuNRs@*m*SiO_2 before and after Hg amalgamation were determined using SEM images, and the structural alterations were investigated. The structural alterations on amalgamated single AuNRs@*m*SiO_2 were then examined in relation to varied oxygen plasma exposure times.

Furthermore, using SEM and an energy dispersive X-ray spectrometer (EDX), elemental mapping pictures of amalgamated AuNRs@*m*SiO_2 were obtained.

Oxygen Plasma Treatment. A plasma cleaner (PDC-32G-2, Harrick Plasma, USA) was used to execute the oxygen plasma treatment. All oxygen plasma treatments were conducted with a maximum RF power of 18W at various plasma treatment times of 0, 3, 5, 10, 15, and 20 min.

Scattering-based DF Microscopy. An inverted Nikon microscope (Nikon Eclipse Ti-2) was used to perform DF microscopy imaging. In DF mode, the microscope used a Nikon Plan Fluor 100 × 0.5-1.3 oil iris objective (NA = 0.7–1.4). An inverted Nikon DF condenser (NA = 0.7–1.4). An Andor iXon EMCCD camera (iXon Ultra 897) was used to capture detailed DF scattering images of desired nanoparticles. The collected images were analyzed using ImageJ and Matlab.

Single-Particle Scattering Spectroscopy. DF scattering spectra of single AuNRs@*m*SiO_2 and Hg amalgamated AuNRs@*m*SiO_2 were acquired with an Andor spectrophotometer (SHAMROCK 303i, SR-303I-A) connected with an Andor CCD camera (Newton DU920P-OE). The single-particle scattering spectrum was acquired by shifting the scanning stage to the appropriate sample location, allowing the objective to gather only the scattered light from the selected nanoparticle. The scattered light from a single nanoparticle was directed to a spectrophotometer, where it was dispersed by a grating (300 l/mm) and detected by a Newton CCD camera (center wavelength of 700 nm). The background was measured in a particle-free environment. Data analysis was performed using custom-made Matlab scripts.

Additional Discussion

The Au and Hg Interaction Mechanism. Due to the strong affinity between Au and Hg, the liquid Hg formed in the solution chemisorbed on the Au surface initially and then forms a surface metallic layer of Hg. The presence of the Hg surface layer facilitates the alloy structure formation of Au-Hg as in the following equation.[1]

$$2Hg(l) + Au(s) \rightarrow AuHg_2 (l)$$

Due to the low Hg cohesive energy (0.67 eV/atom) compared to Au (3.81 eV/atom), the Au–Hg alloy formation is facilitated by dissolution and diffusion of Au atom into Au/Hg interface or Hg layer up to a certain degree. This is observed in changes of LSPR peak energy and linewidth as discussed in this work.

References

1) M. Rex, F. E. Hernandez and A. D. Campiglia, *Anal. Chem.*, 2006, **78**, 445-451.

Supplementary Figures

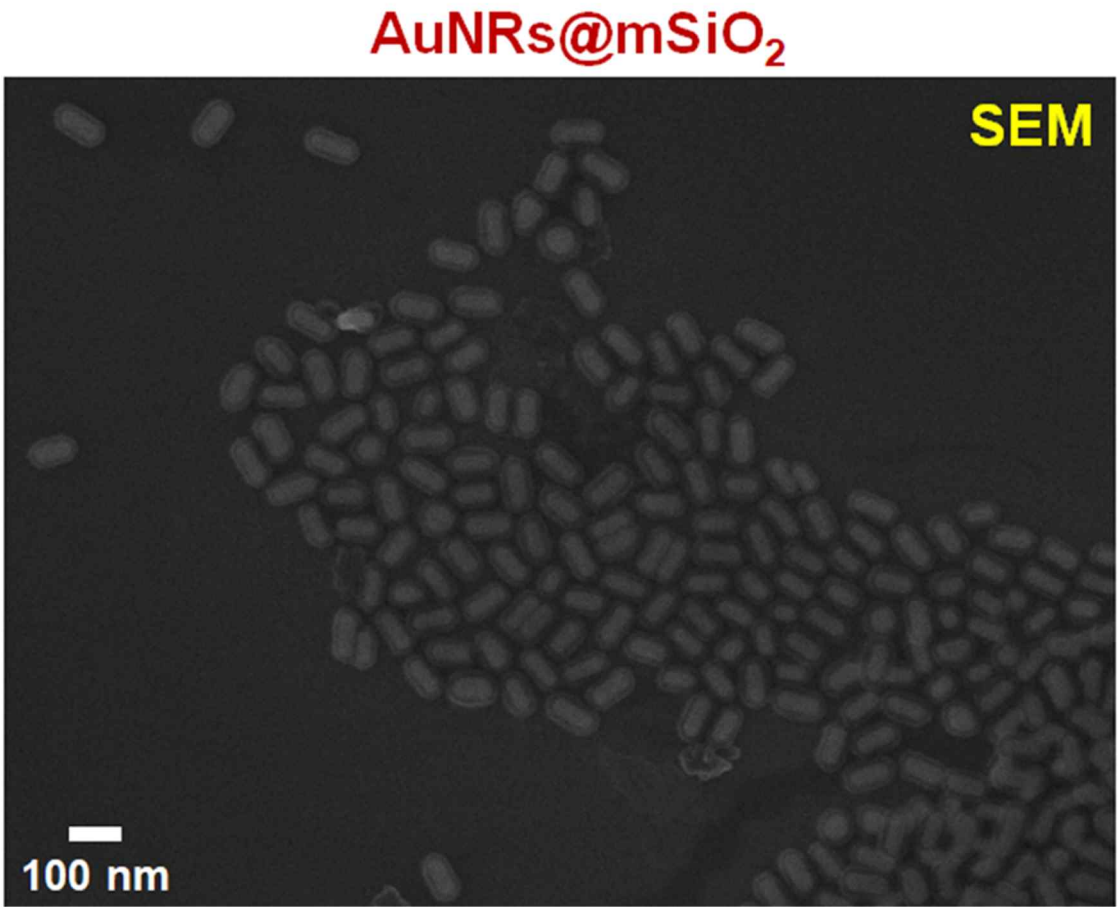

Fig. S1 SEM image of AuNRs@*m*SiO_2 (before the Hg amalgamation).

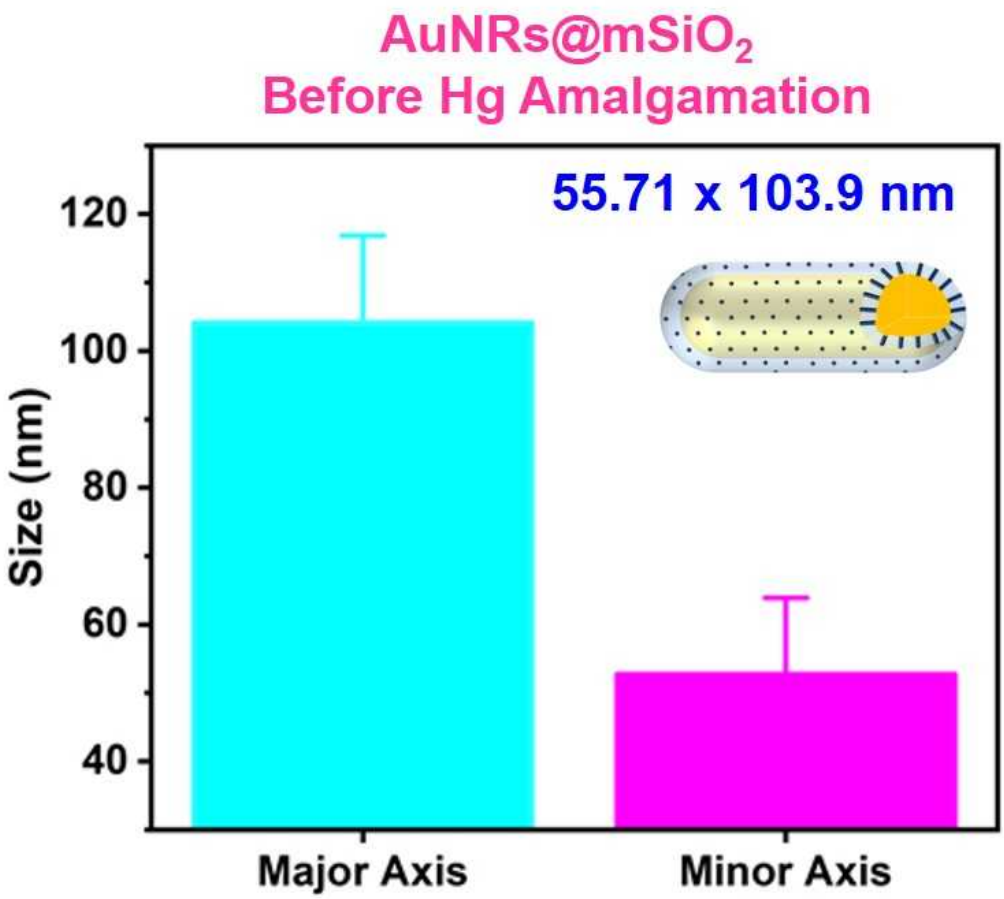

Fig. S2 Bar graph to show average size of major axis (length) and minor axis (diameter) of AuNRs@*m*SiO_2 after amalgamation in Hg solution for 1 h.

Fig. S3 SEM image to show the silica shell thickness of AuNR@*m*SiO_2. A thickness was determined to be about 19 nm.

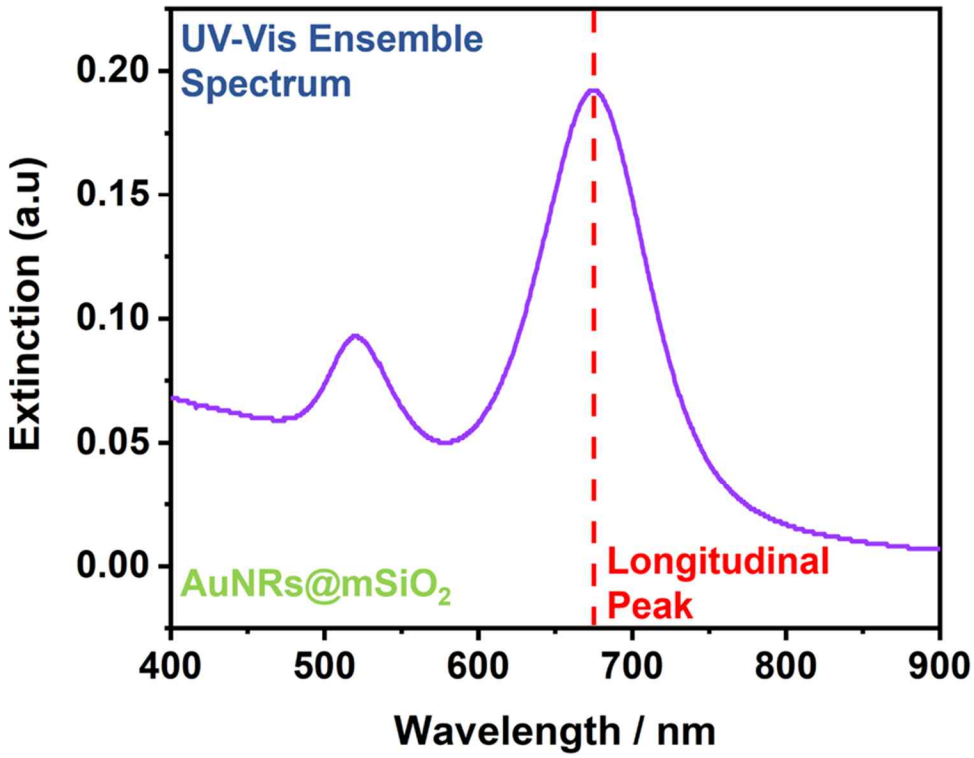

Fig. S4 UV-Vis extinction spectra of AuNRs@*m*SiO_2 dispersed in water, showing two distinctive transverse and longitudinal LSPR peaks.

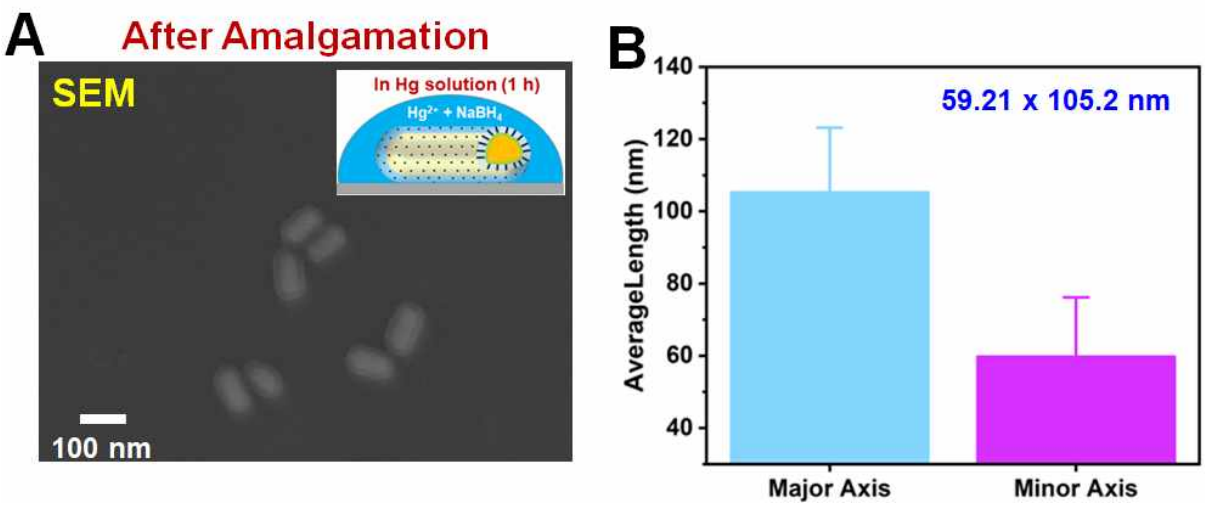

Fig. S5 (A) SEM image of AuNRs@*m*SiO_2 after amalgamation in Hg solution for 1 h. **(B)** Bar graph to show the average size of major (length) axis and minor axis (diameter) of AuNRs@*m*SiO_2 after Hg amalgamation.

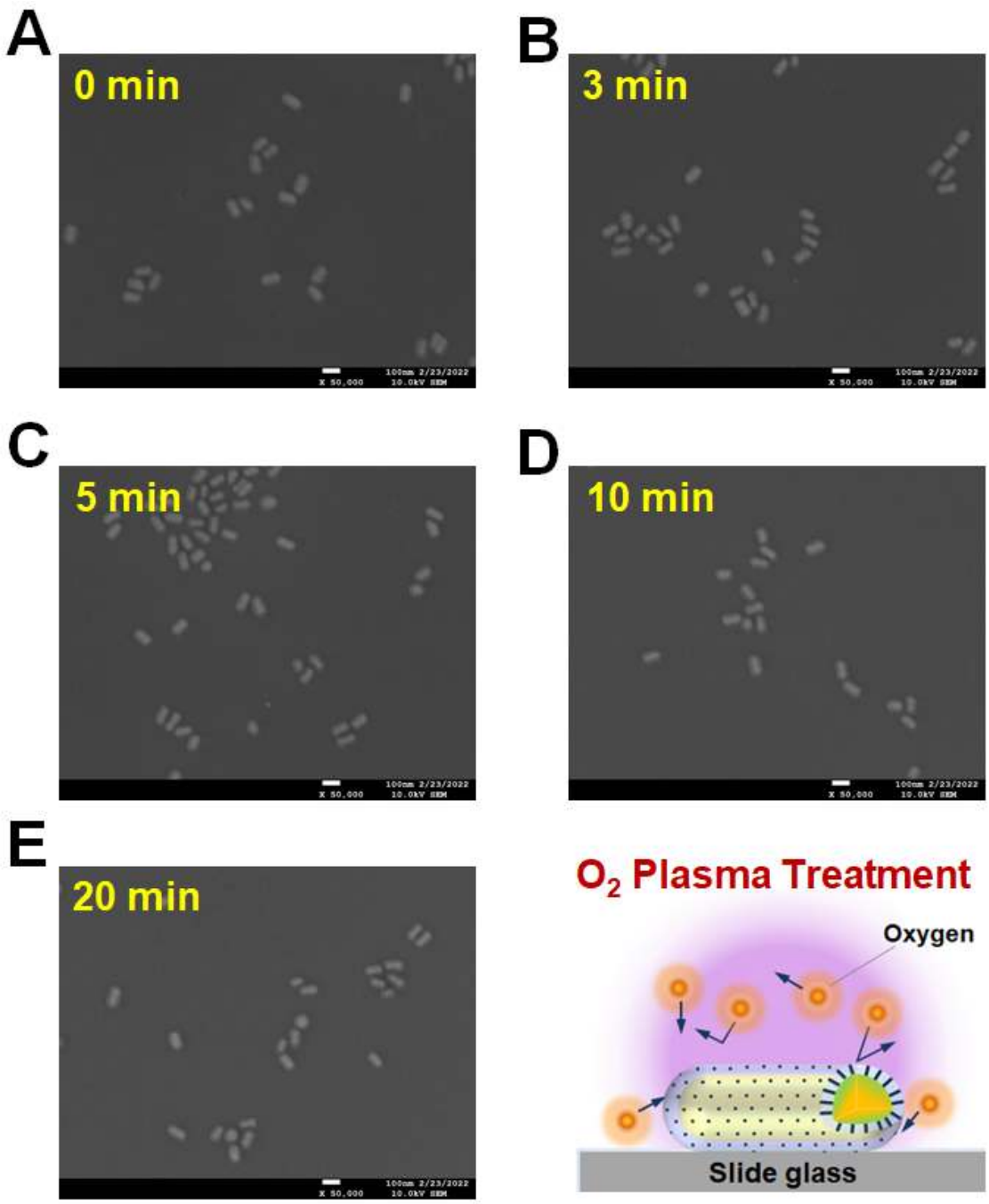

Fig. S6 SEM images showing Hg amalgamated AuNRs@*m*SiO_2 at different oxygen plasma treatment times of **(A)** 0, **(B)** 3, **(C)** 5, **(D)** 10, and **(E)** 20 min, respectively.

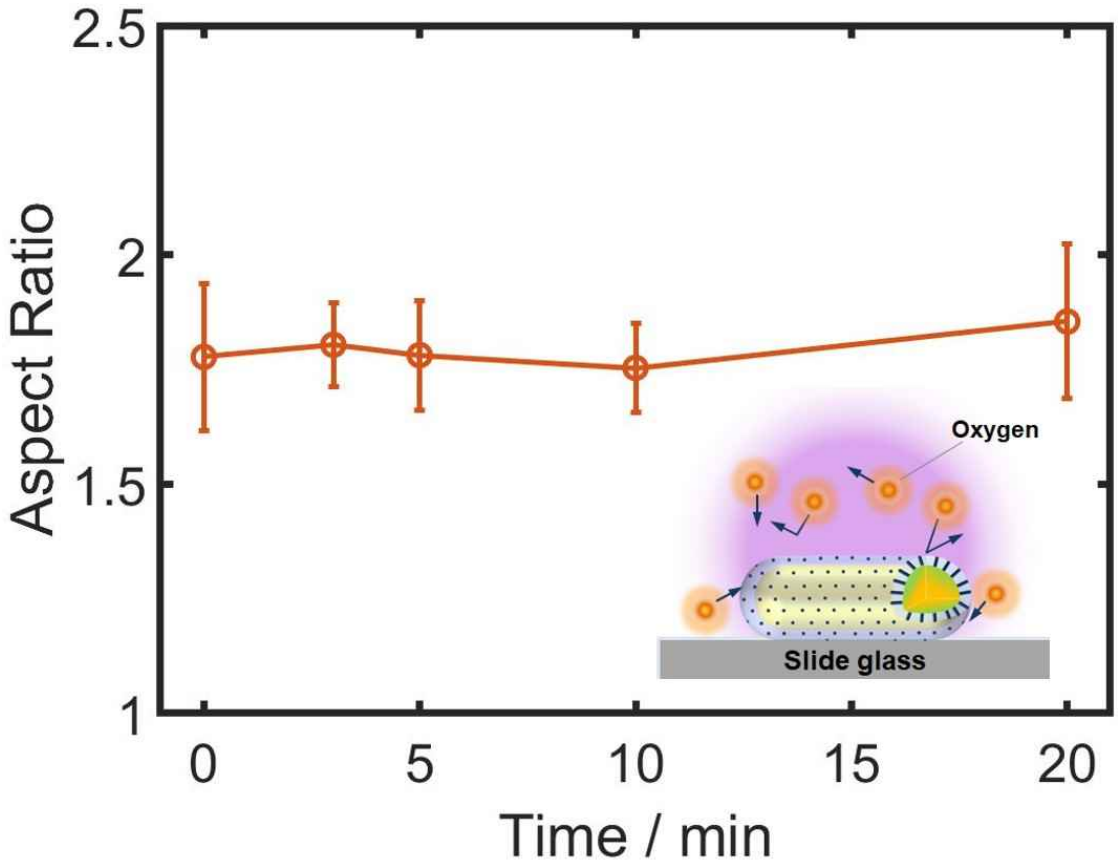

Fig. S7 A graph to show the change in average AR of amalgamated AuNRs@*m*SiO_2 at different oxygen plasma treatment times of 1, 3, 5, 10, and 20 min.

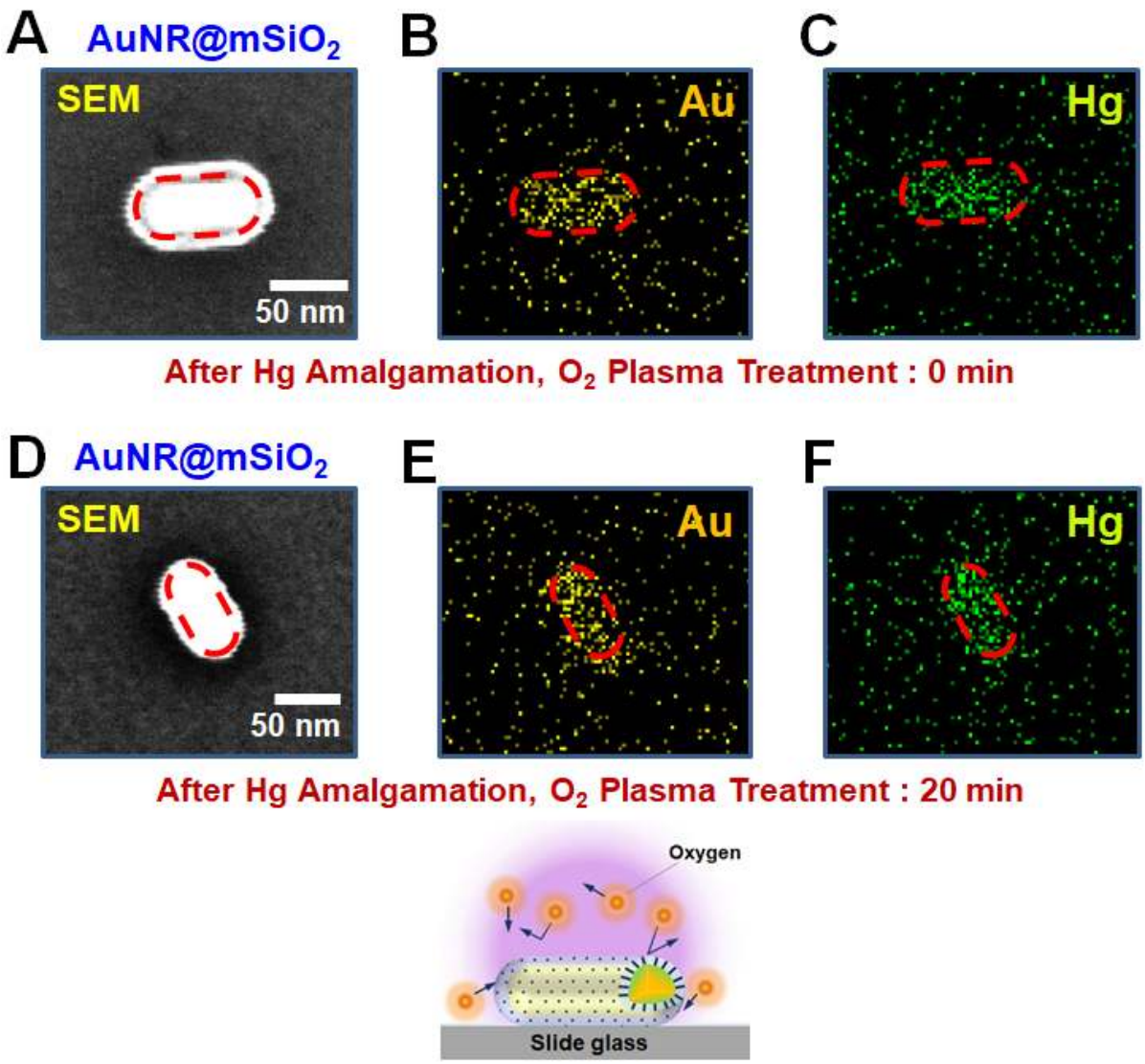

Fig. S8 SEM with EDX elemental mapping analysis of amalgamated AuNRs@*m*SiO_2 before and after oxygen plasma treatment. **(A–C)** Enlarged SEM image and corresponding elemental mapping images of (B) Au and (C) Hg in single amalgamated AuNR@*m*SiO_2 before plasma treatment (0 min). **(D–F)** Enlarged SEM image and corresponding elemental mapping image of (E) Au and (F) Hg single amalgamated AuNR@*m*SiO_2 after 20 min of oxygen plasma treatment.

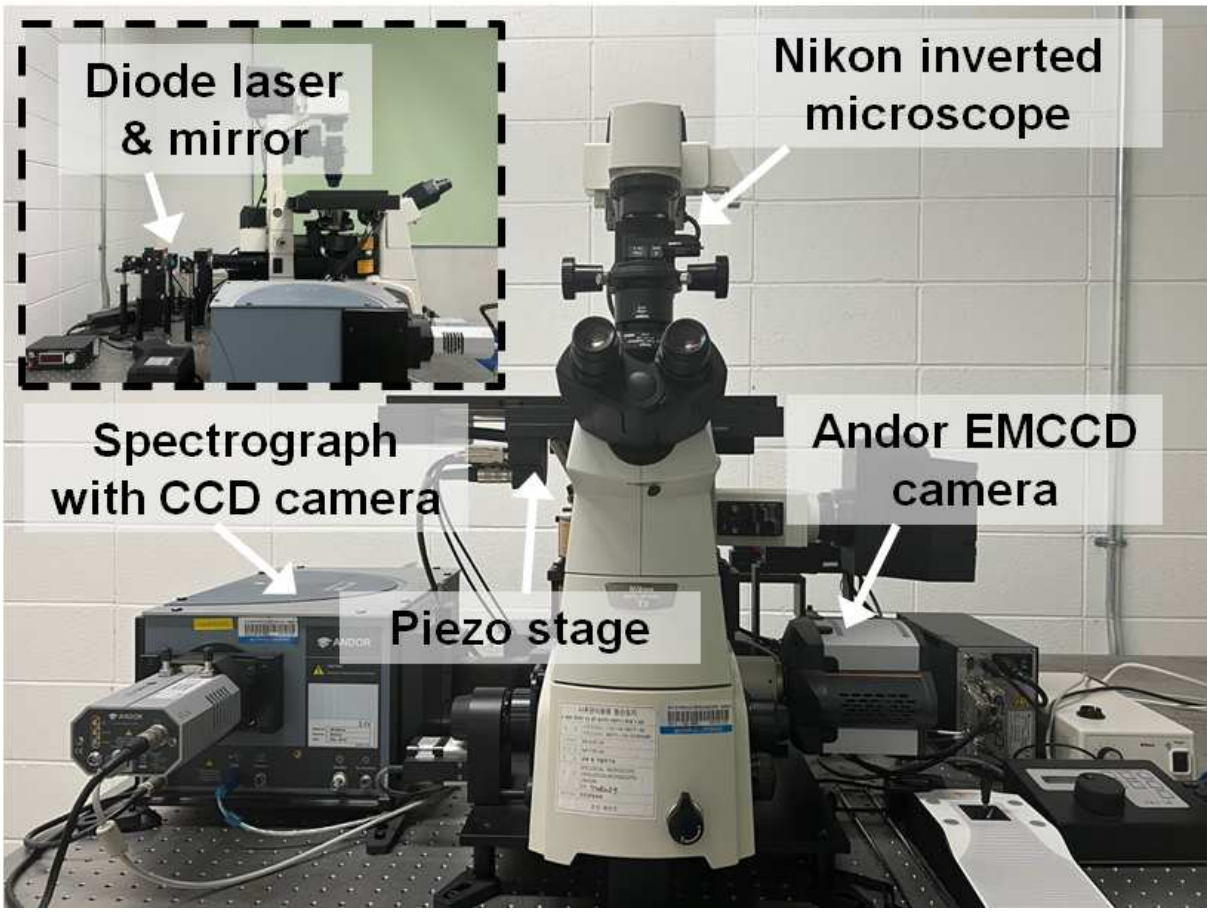

Fig. S9 A photograph showing the experimental setup for single-particle DF microscopy and spectroscopy

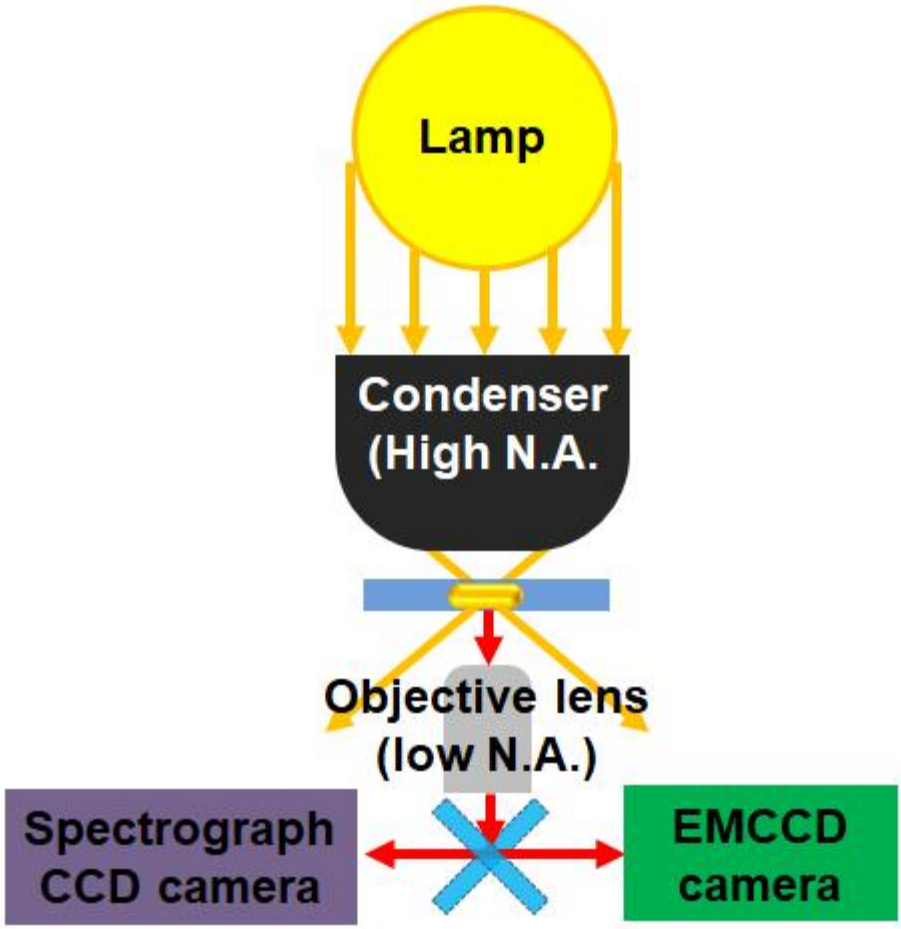

Fig. S10 Schematic to show a working principle of DF microscopy and spectroscopy

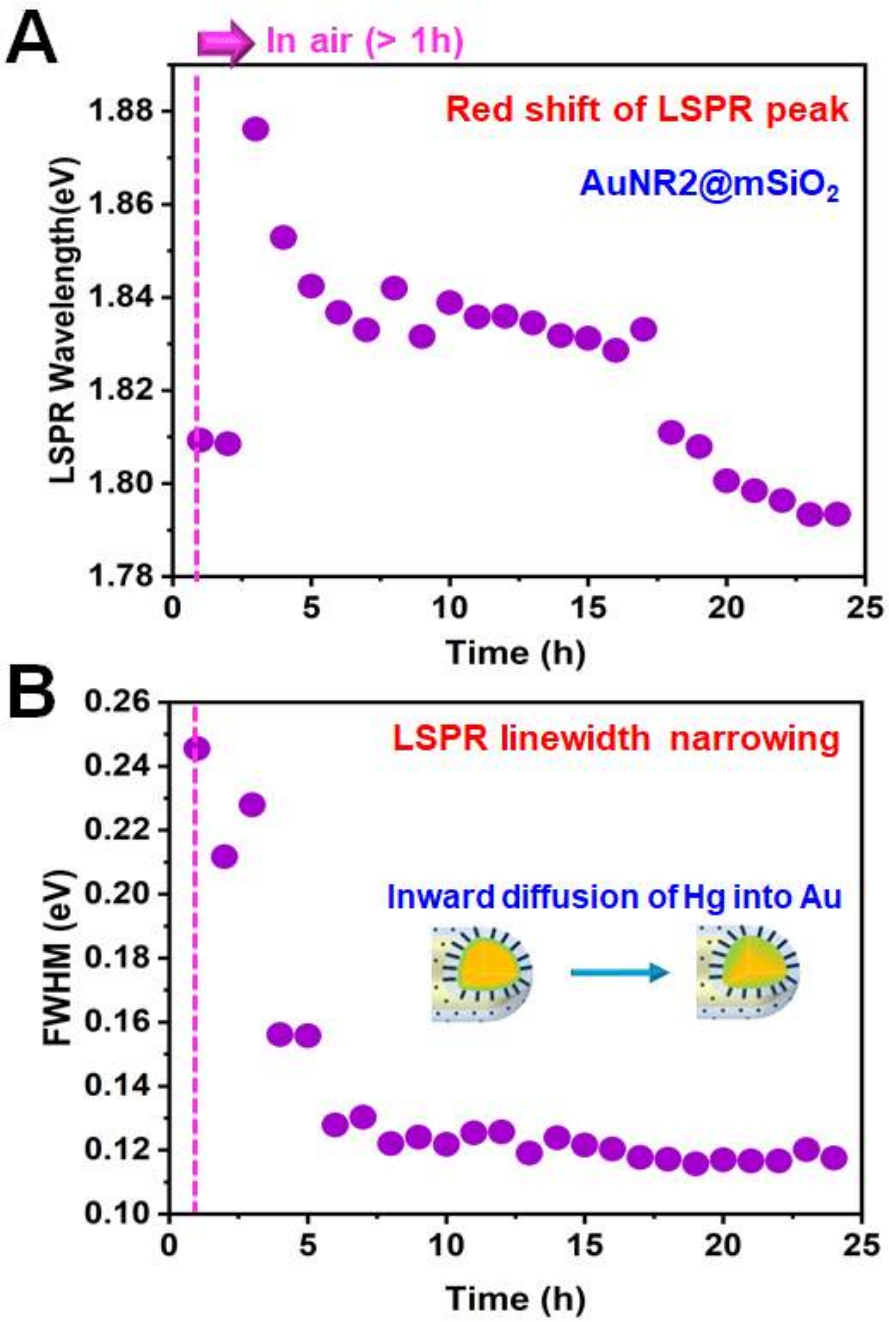

Fig. S11 (A) Time-dependent change of the LSPR peak of AuNR2@*m*SiO_2 (in Fig. 4A) taken out from Hg solution (after 1 h) and exposed to air as a function of time. **(B)** Change in the corresponding FWHM of AuNR2@*m*SiO_2 as a function of time. Scattering spectrum was obtained at intervals of 1 h.

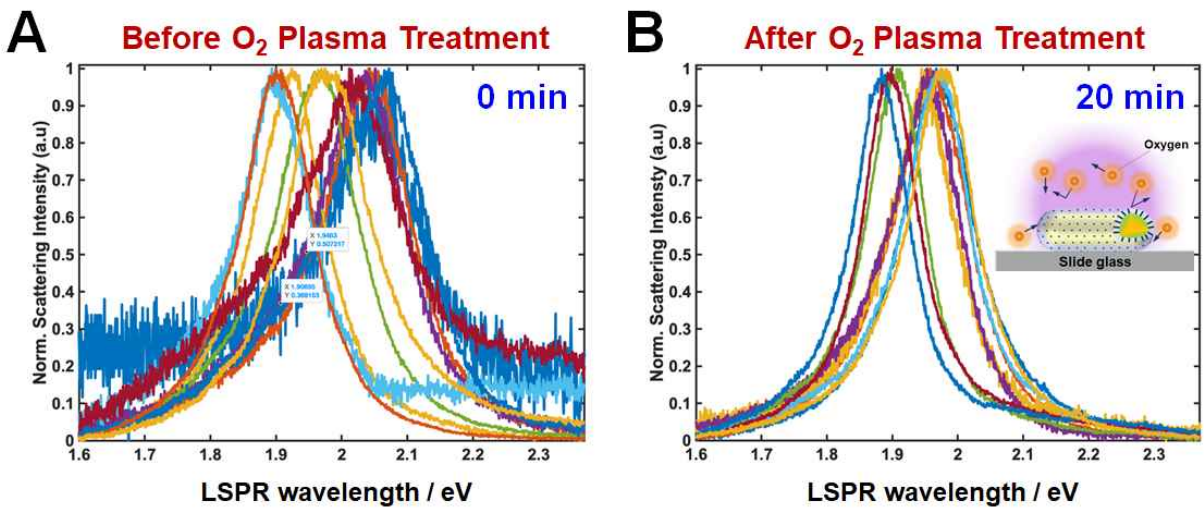

Fig. S12 Single-particle scattering spectra of amalgamated AuNRs@*m*SO_2 **(A)** before oxygen plasma treatment and **(B)** after oxygen plasma treatment for 20 min.