Electronic Supplementary Information

for

Single-Particle Study: Effects of Mercury Amalgamation on Morphological and Spectral Changes in Anisotropic Gold Nanorods

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Experimental Methods

Materials and Sample Preparation. Hg(II) chloride and sodium borohydride ($NaBH_4$) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Cetyltrimethylammonium bromide (CTAB)-stabilized AuNRs (25 nm × 73 nm) were purchased from Nanopartz (Loveland, CO, USA). The microscope cover glasses were obtained from Sigma-Aldrich. The microscope cover glass and slide glass were cleaned by sonicating in ethanol, distilled water, and isopropanol for 15 min, respectively. The solution containing the AuNRs was diluted 15 times and sonicated for 15 min to prevent the aggregation of the nanoparticles. The diluted AuNR solution was drop-casted onto the pre-cleaned glass slide and allowed to dry. The concentration of AuNRs on the slide glass surface was controlled to be 1 μm^{-2} in order to characterize single AuNRs and to minimize the inter-particle LSPR coupling.

Structural Characterization. After the samples (AuNRs@AuHg after amalgamation) were treated with oxygen plasma, their structural characterizations were carried out using a scanning electron microscope (SEM, JSM-6500F, JEOL, Japan). We then checked the structural changes of single AuNRs@AuHg from the SEM images and determined their length and width. Additionally, the elemental mapping images of AuNRs@AuHg were obtained using high-resolution transmission electron microscopy (HR-TEM, JEM-2100F, JEOL, Japan) and SEM combined with energy dispersive X-ray spectrometer (EDX). We further checked the additional structural changes of AuNRs@AuHg not treated with oxygen plasma and took their TEM images after 7 days using field emission transmission electron microscopy (FE-TEM, Tecnai G2 F20 X-Twin, FEI, USA).

Oxygen Plasma Treatment. The oxygen plasma treatment was performed using a plasma cleaner (PDC-32G-2, Harrick Plasma, USA). All oxygen plasma treatments were carried out with a maximum RF power of 18W at various plasma treatment times of 0, 1, 3, 5, 10, 15, and 20 min.

Total Internal Reflection Scattering (TIRS) Microscope. The excitation of TIRS microscope was done using an inverted Nikon microscope (Nikon Eclipse Ti-2) with Halogen lamps as an excitation source (Fig. S4). The TIRS microscopy, the beam from the halogen lamp source passed through an optical fiber with the core diameter of 100 mm. Two collimating lenses for the optical fiber were used at the opposite ends of the optical fiber. Incident light was directed into samples by a glass prism, and the incident angle was maintained at 70°. The microscope utilized a Nikon Plan Fluor oil objective (100×, NA 0.5-1.3), and the NA of the objective was maintained at 0.7. An Andor iXon^{EM}+CCD camera (iXon897) was employed to record TIRS images of AuNPs The collected images were analyzed by ImageJ and Matlab..

Total Internal Reflection Scattering (TIRS) Spectroscopy. Scattering spectra were acquired with a spectrometer (Andor, Kymer328i-A) and a CCD camera (Andor, Newton920) (Fig. S4). We mounted a relay lens system [a Newton lens system with two lenses (f=7 cm)] between the microscope and the spectrometer system. The scattered light by AuNR@AuHg was dispersed by a grating (300 l/mm), and detected by the CCD camera. To measure the background, a region without any particles was selected. The single particle scattering spectra of AuNRs were fitted to a Lorentzian function to measure their LSPR linewidth and the resonance peak energy.

Supplementary Figures

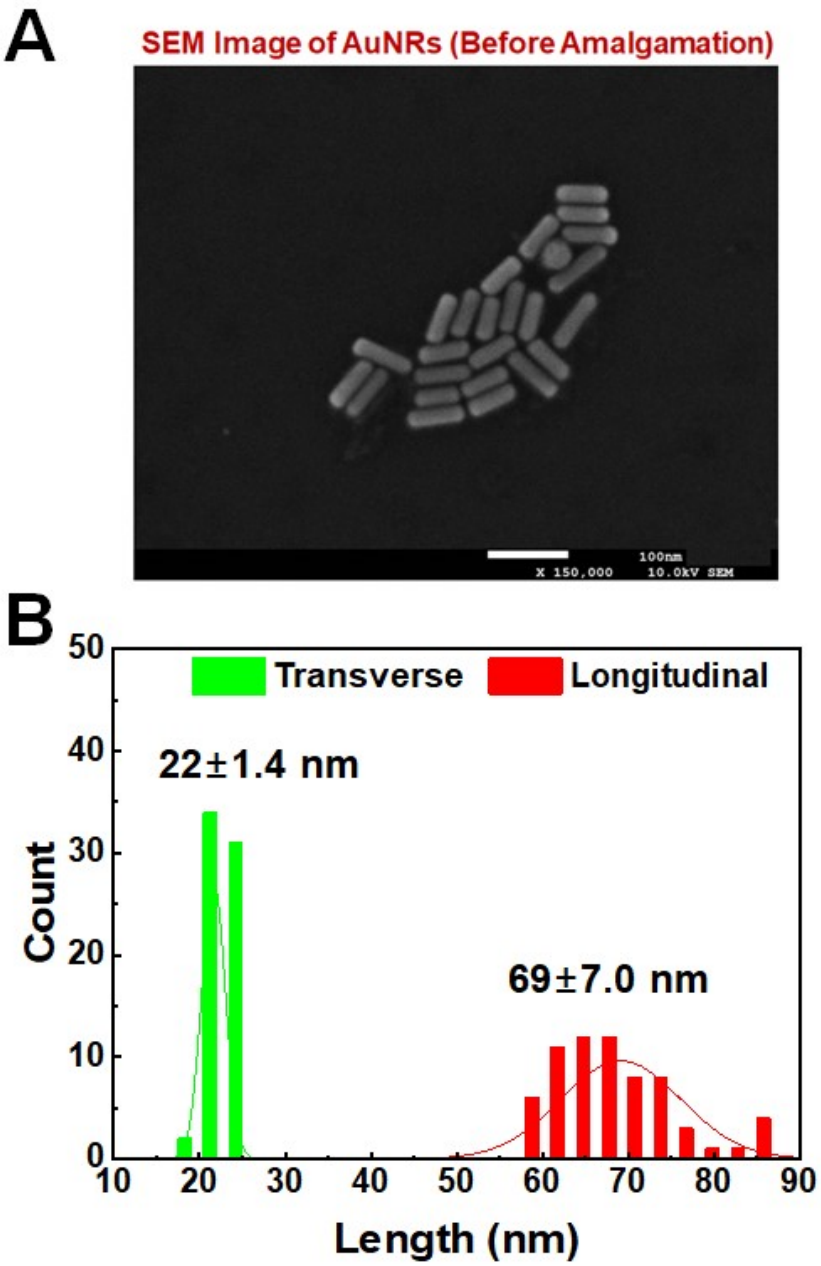

Fig. S1 (A) SEM image of AuNRs (before the amalgamation). **(B)** Histogram to show the size of AuNRs in two longitudinal and transverse axes. The sizes of AuNRs were determined by their SEM images.

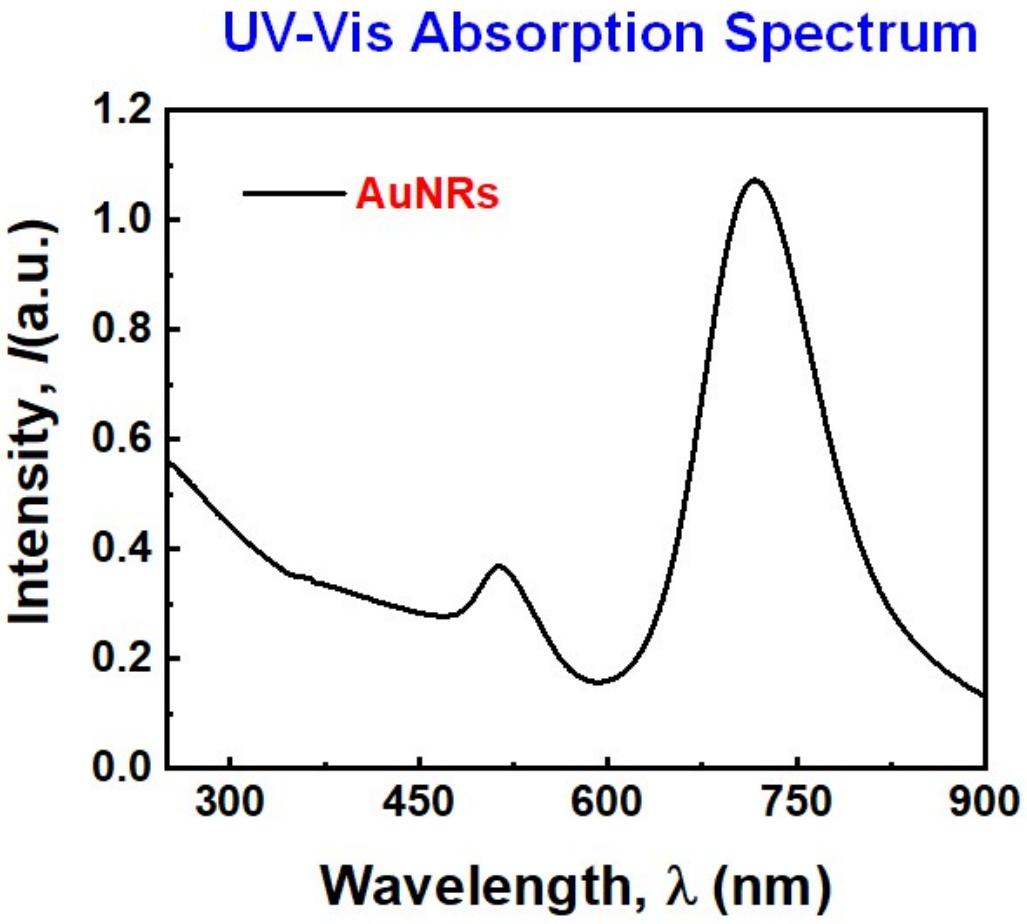

Fig. S2 UV-Vis absorption spectrum of AuNRs obtained from Nanopartz (before amalgamation).

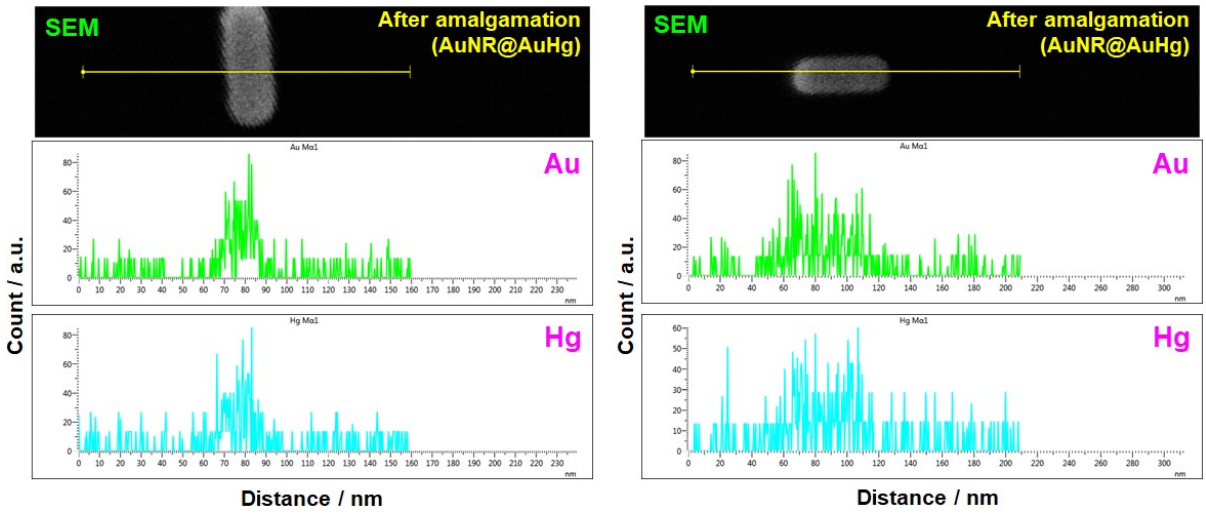

Fig. S3 SEM with EDX image mapping analysis of AuNRs after Hg amalgamation (AuNRs@AuHg). Enlarged SEM images of single AuNRs and line scanning to show Au and Hg elements are provided.

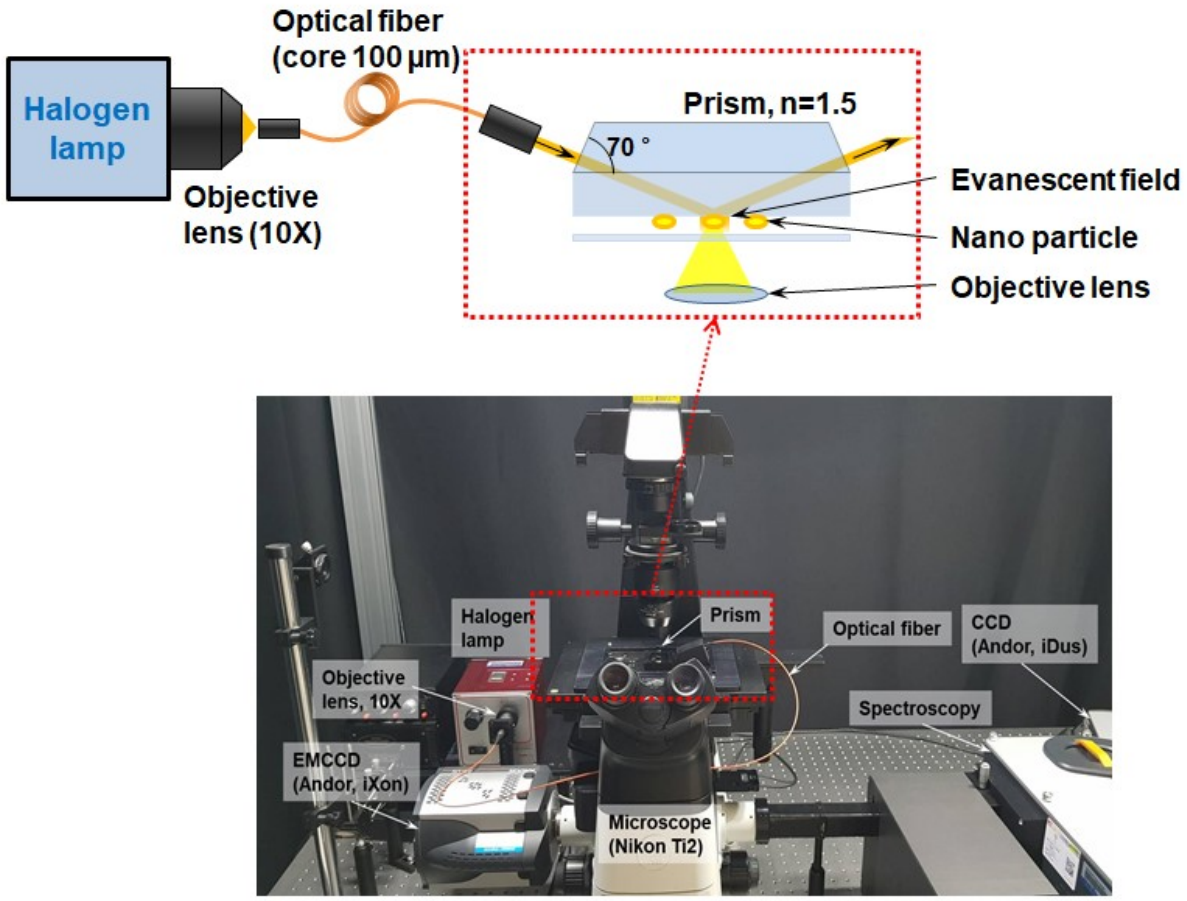

Fig. S4 A photograph showing the experimental setup for single particle TIRS microscopy and spectroscopy. In addition, schematic diagram shows illumination using halogen lamp (white light source) in TIRS microscopy based on the evanescent field at the interface.

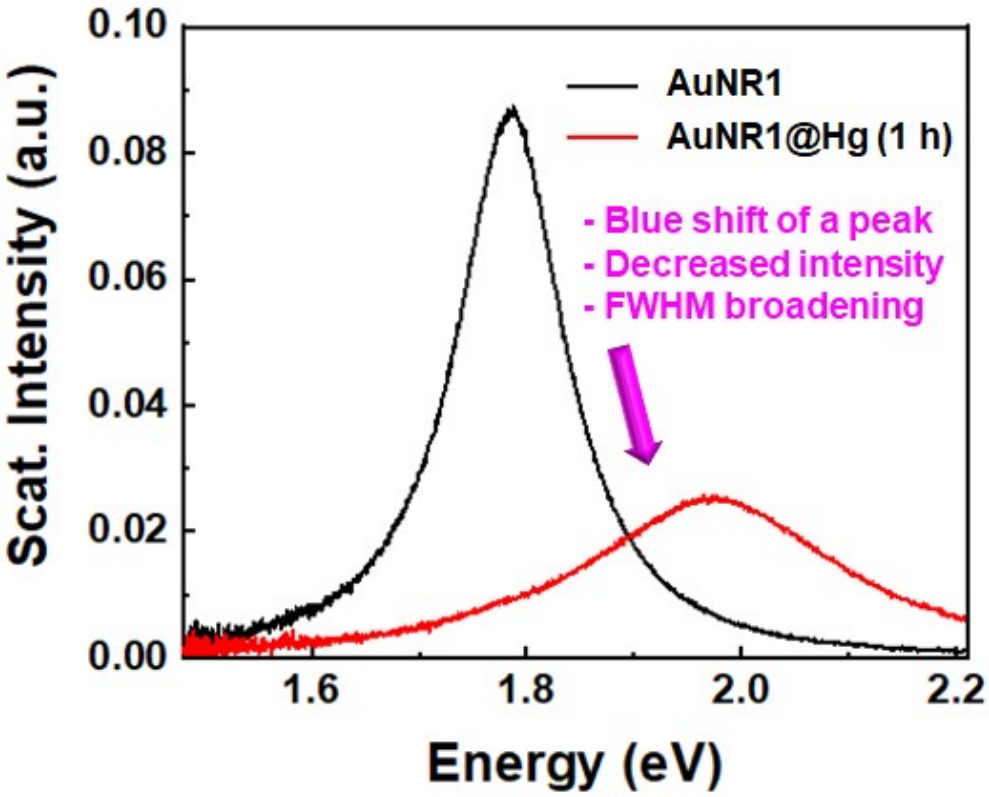

Fig. S5 Scattering spectra of AuNR1 (in Fig. 3A) before exposure to Hg solution (black curve) and after exposure to Hg solution for 1 h (red curve). A strong decrease in the scattering intensity with FWHM broadening is observed after Hg adsorption on the AuNR1 (AuNR1@Hg).

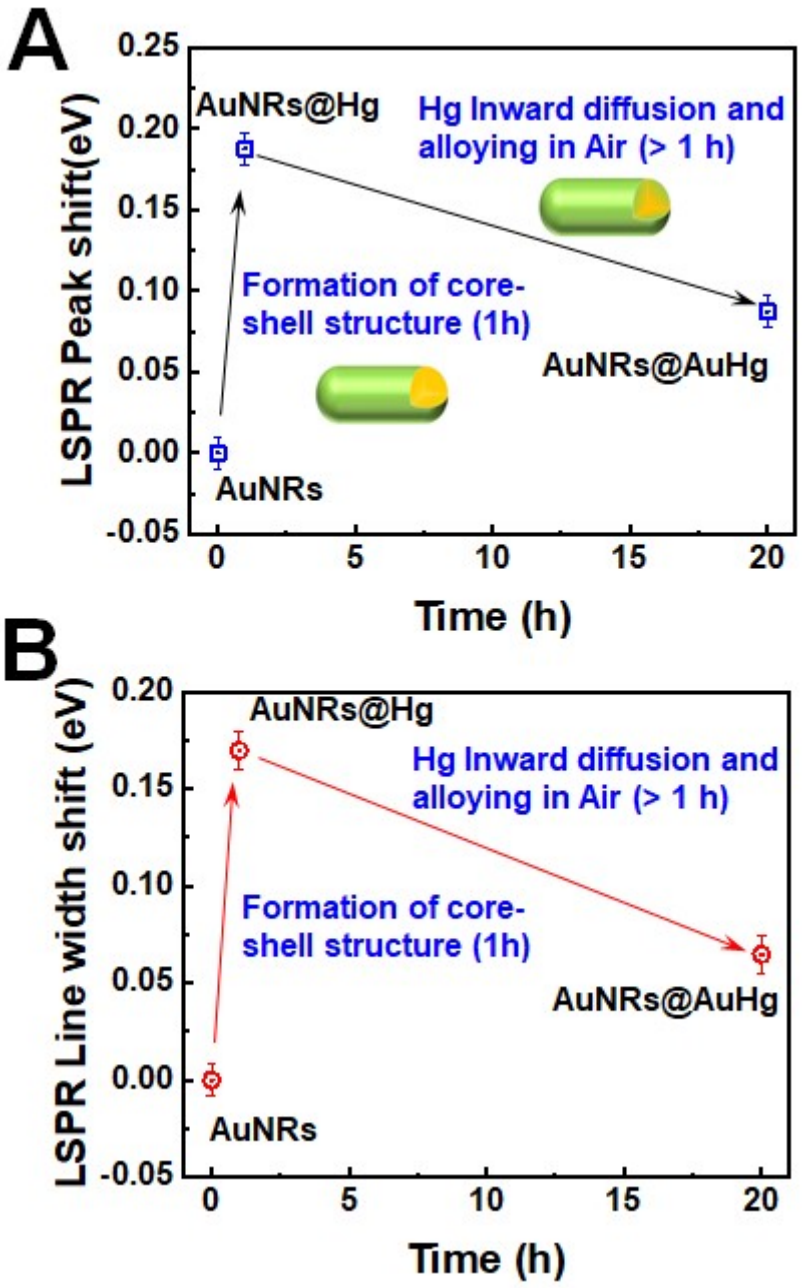

Fig. S6 (A) Change in the LSPR peak of AuNRs exposed to Hg solution over time. After 1 h, AuNRs were exposed to air and measured after 20 h. **(D)** Change in the corresponding LSPR linewidth of AuNRs in (A).

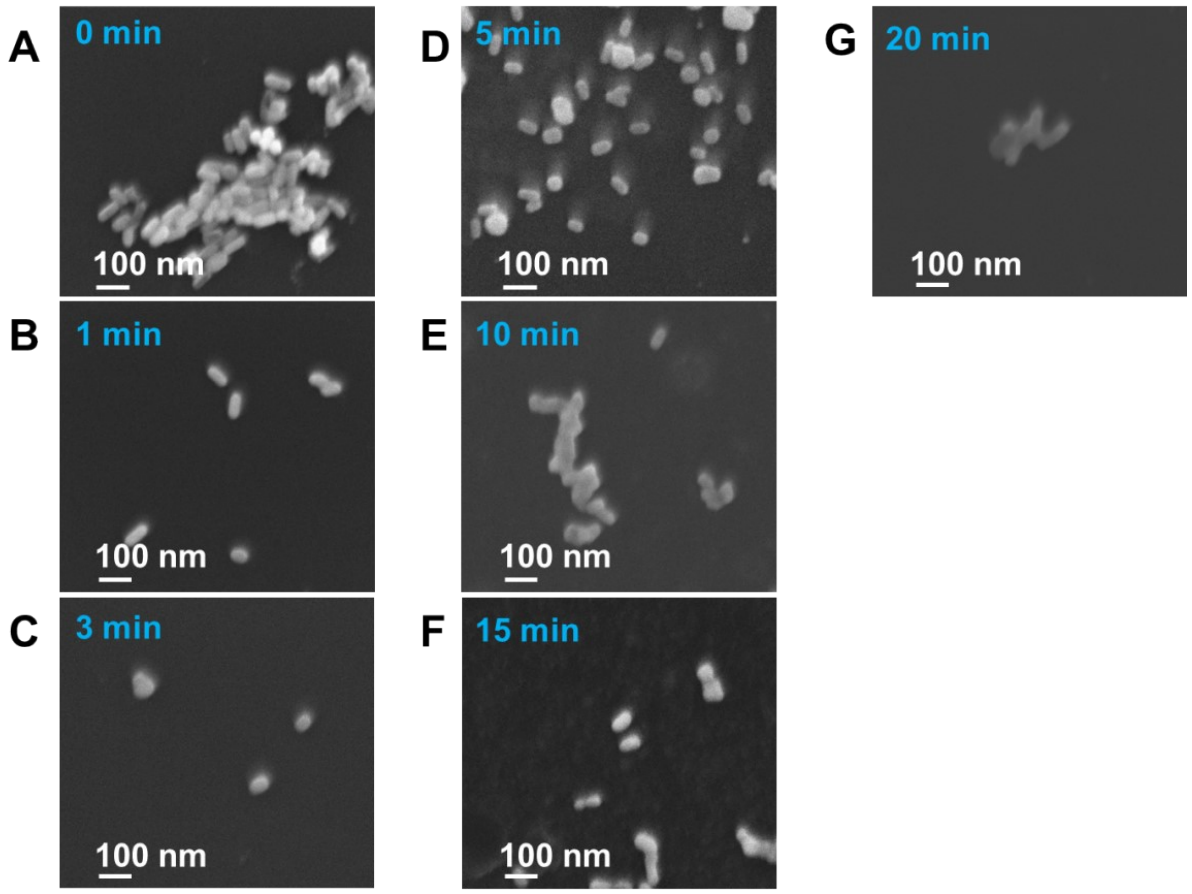

Fig. S7 SEM images of AuNR@AuHg **(A)** before and **(B-G)** after the oxygen plasma treatment at various times of 0, 1, 3, 5, 10, 15, and 20 min.

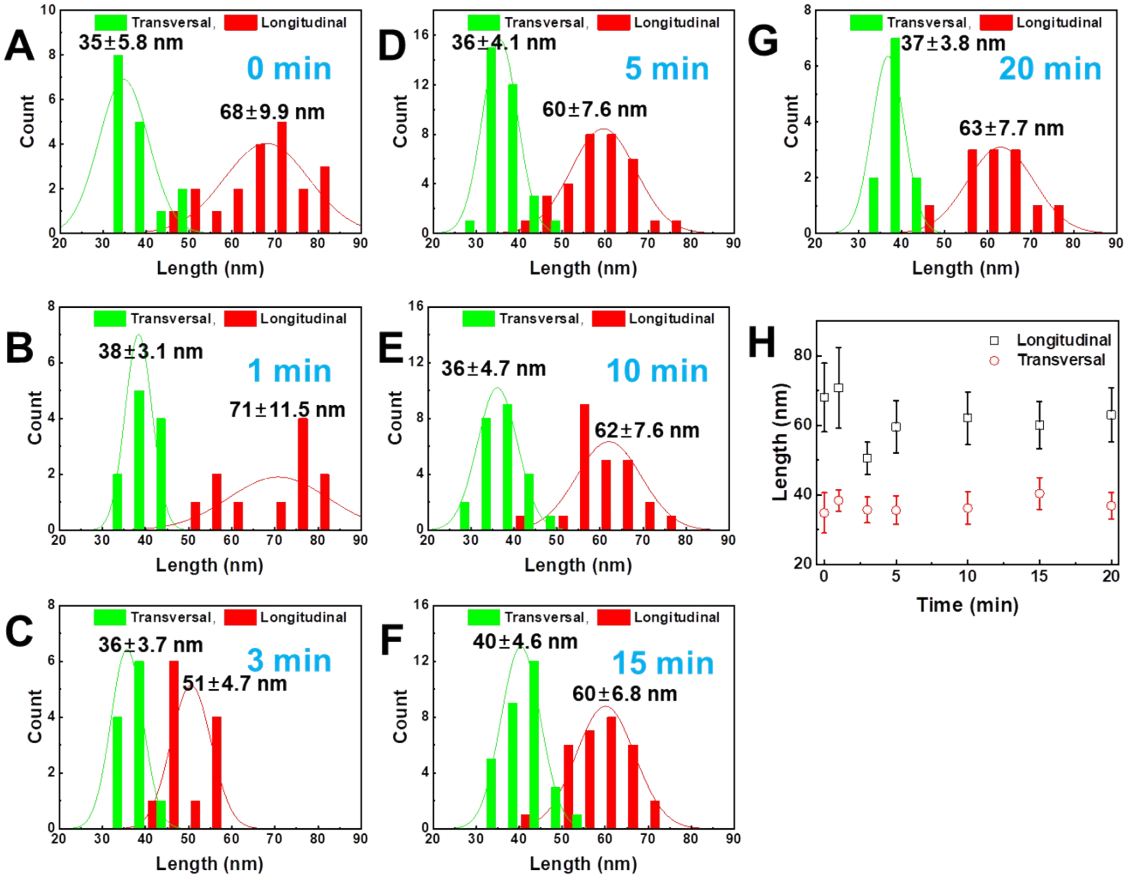

Fig. S8 (A-G) Changes in the sizes of AuNRs@AuHg by the oxygen plasma treatment at different treatment times. **(H)** A graph to show the changes in sizes (length and width) of AuNRs@AuHg after different oxygen plasma treatment times.