Electronic Supplementary Information

In Situ Reversible Tuning of Chemical Interface Damping in Mesoporous Silica-Coated Gold Nanorods *via* Direct Adsorption and Removal of Thiol

Yun A Hong[1] and Ji Won Ha[1,2]*

[1]Department of Chemistry, University of Ulsan, 93 Daehak-ro, Nam-gu, Ulsan 44610, Republic of Korea

[2]Energy Harvest-Storage Research Center (EHSRC), University of Ulsan, 93 Daehak-ro, Nam-gu, Ulsan 44610, Republic of Korea

*To whom correspondence should be addressed

J. W. Ha

Phone: +82-52-712-8012

Fax: +82-52-712-8002

E-mail: jwha77@ulsan.ac.kr

Experimental Methods

Materials and Sample Preparation. AuNRs@mSiO_2 used in this study were purchased from Nanopartz (Loveland, CO, USA). The microscope cover glasses were obtained from Sigma-Aldrich (St. Louis, MO, USA). The microscope cover glass and glass slide were cleaned *via* consecutive sonication in ethanol, distilled water, and isopropanol for 15 min. The solution containing the AuNRs@mSiO_2 was diluted 15 times and sonicated for 15 min to prevent the aggregation of nanoparticles. The diluted AuNRs@mSiO_2 solution was drop-cast onto the pre-cleaned glass slide and allowed to dry. The concentration of AuNRs@mSiO_2 on the glass slide surface was controlled at 1 μm^{-2} to characterize single AuNRs@mSiO_2 and minimize the inter-particle LSPR coupling.

Characterization of AuNRs@mSiO_2. The structure of AuNRs@mSiO_2 was characterized using scanning electron microscopy (SEM, JSM-6500, JEOL, Japan). The LSPR ensemble extinction spectra of AuNRs@mSiO_2 dispersed in water were obtained with a Varian Carry 300 UV-Vis spectrometer (Agilent Technologies).

Sample Preparation for Single-Particle Microscopy and Spectroscopy. The samples for single-particle studies were prepared as follows. First, the colloid AuNRs@mSiO_2 solution was diluted with pure water (18.2 MΩ) to the target concentration. The diluted solution was then sonicated for 10 min at room temperature. Samples were prepared by drop-casting the diluted solution onto pre-cleaned glass slides. This slide was then covered with a 22 mm × 22 mm No. 1.5 coverslip (Corning, NY, USA). In all the experiments conducted in this study, the area density of AuNRs@mSiO_2 deposited on the glass slide was maintained at approximately 1.0 μm^{-2} to facilitate single-particle characterization.

Scattering-based DF Microscopy. DF microscopy was performed using an inverted microscope (Nikon Eclipse Ti-2). In the DF mode, the microscope used a Nikon Plan Fluor 100 × 0.5–1.3 oil iris objective (NA = 0.7–1.4) with 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 the desired nanoparticles. The collected images were analyzed using ImageJ and Matlab.

Single-Particle Scattering Spectroscopy. DF scattering spectra of single AuNRs@*m*SiO_2 were acquired using 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 light scattered by 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. The background was measured in a particle-free environment. Data analysis was performed using custom-made Matlab scripts.

Supplementary Figures

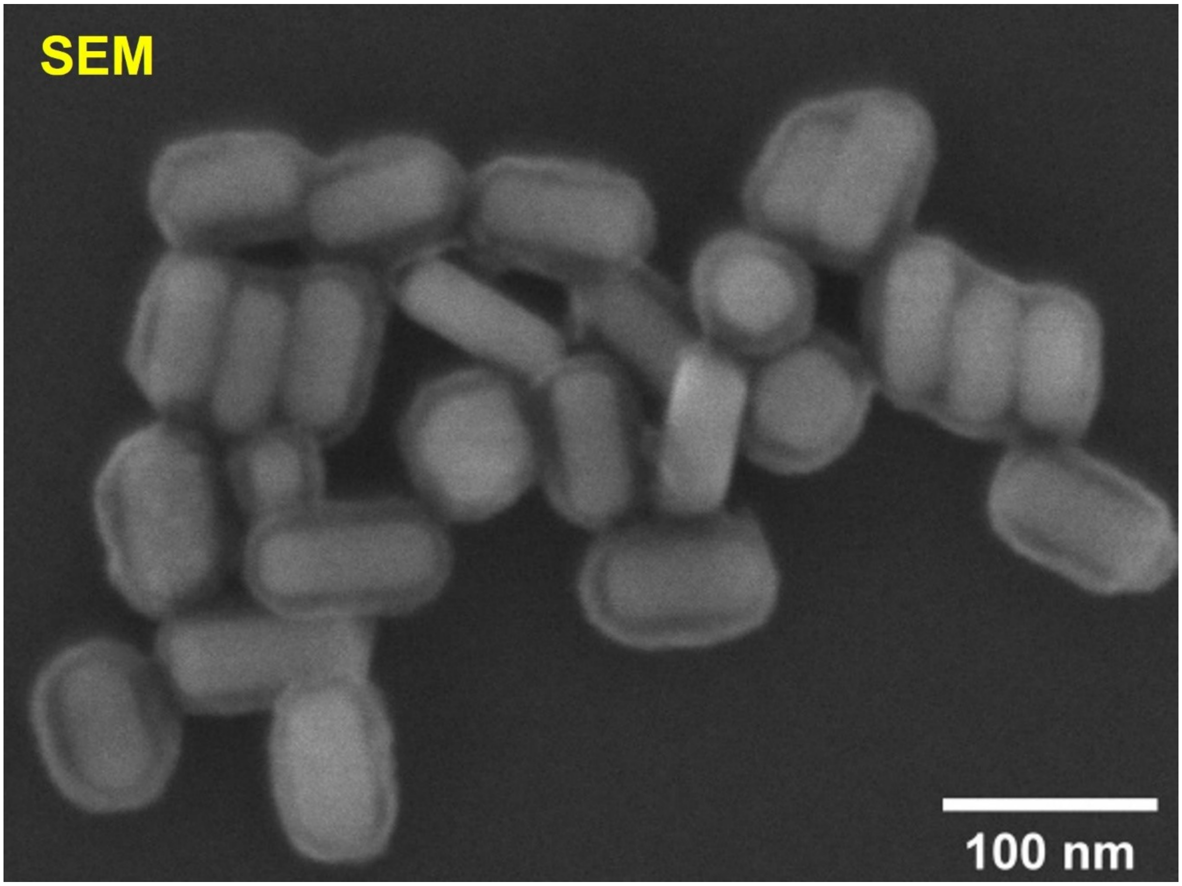

Fig. S1 SEM image of AuNRs@mSiO_2 used in this study.

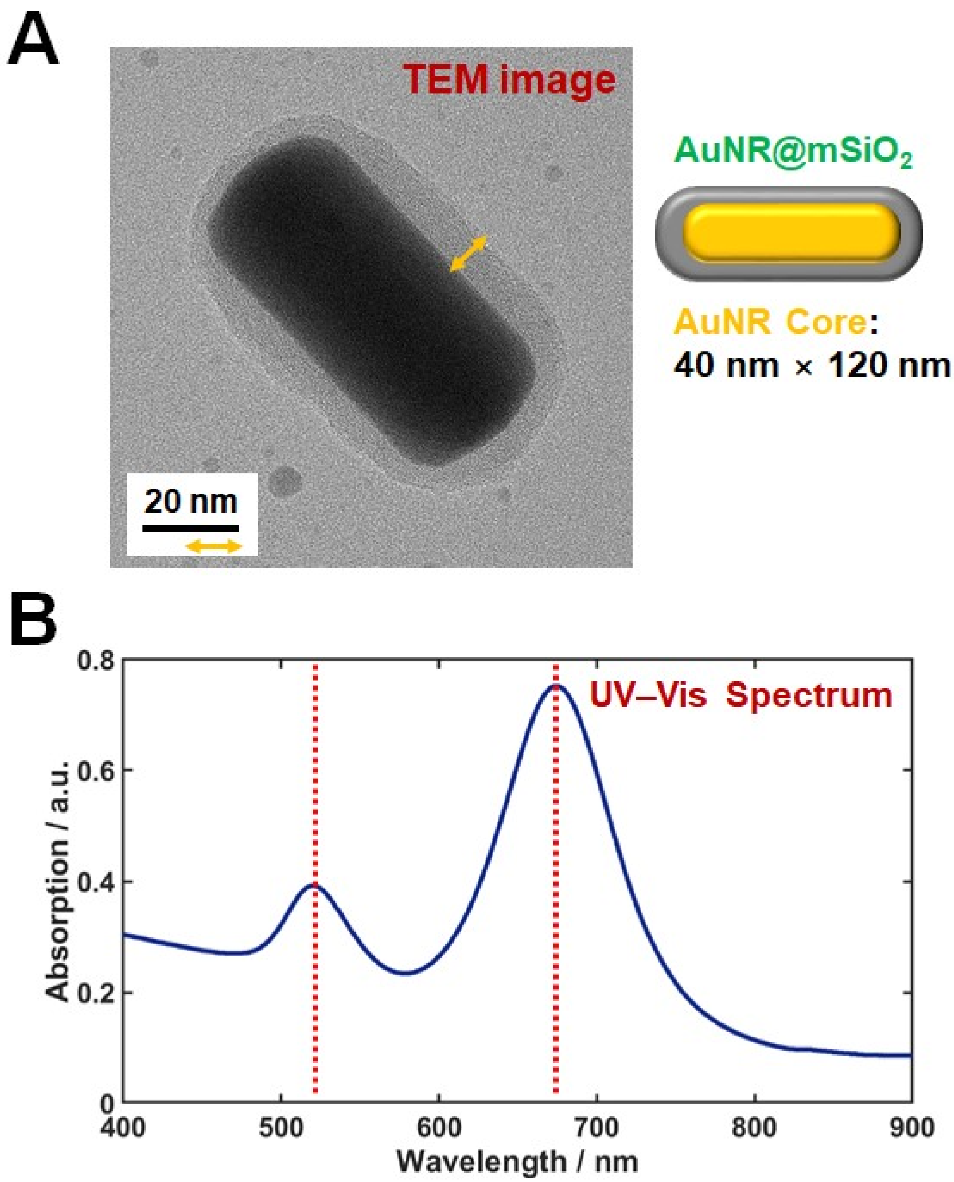

Fig. S2 (A) TEM image to show an AuNR@mSiO_2 and its thickness. **(B)** UV-Vis extinction spectrum of AuNRs@mSiO_2 dispersed in water.

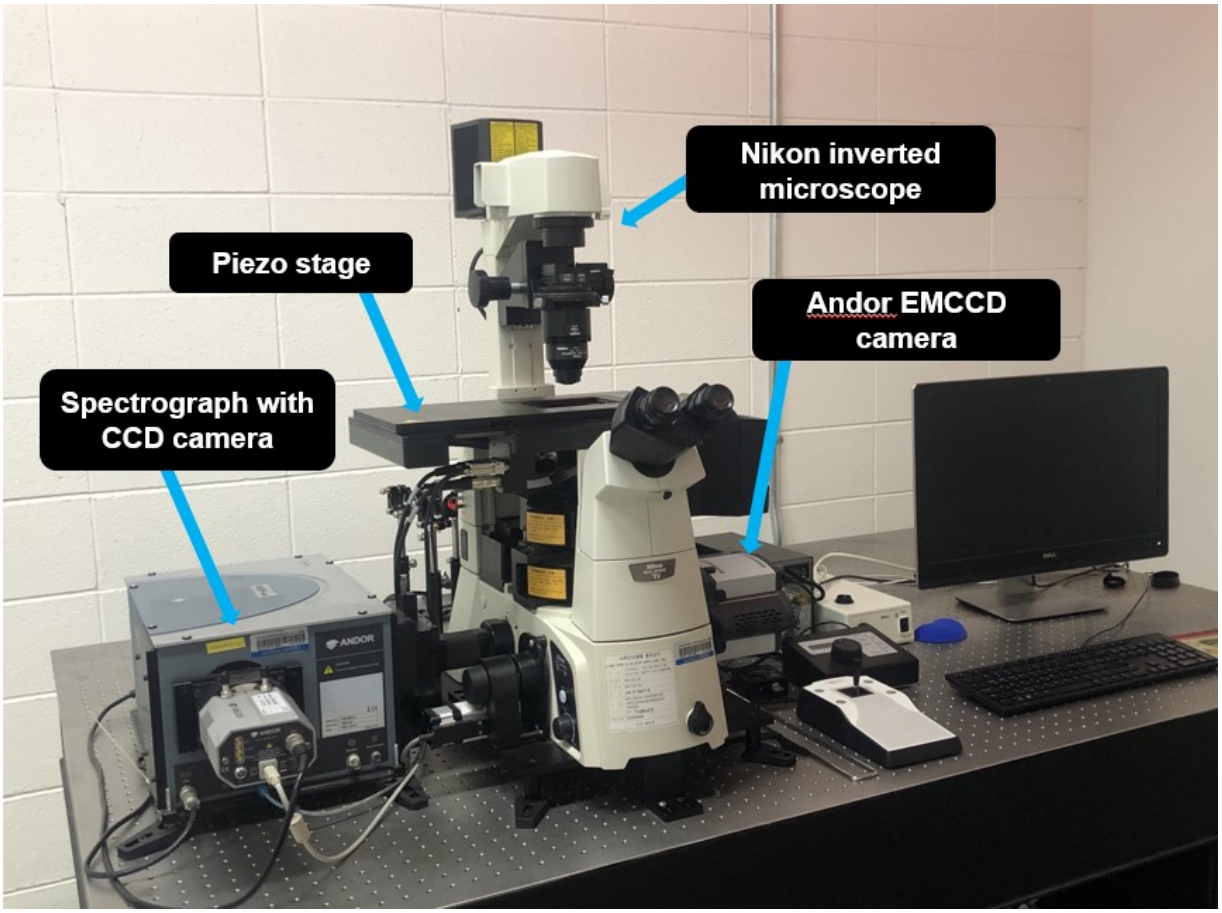

Fig. S3 A photograph showing the experimental setup for single particle DF microscopy and spectroscopy.

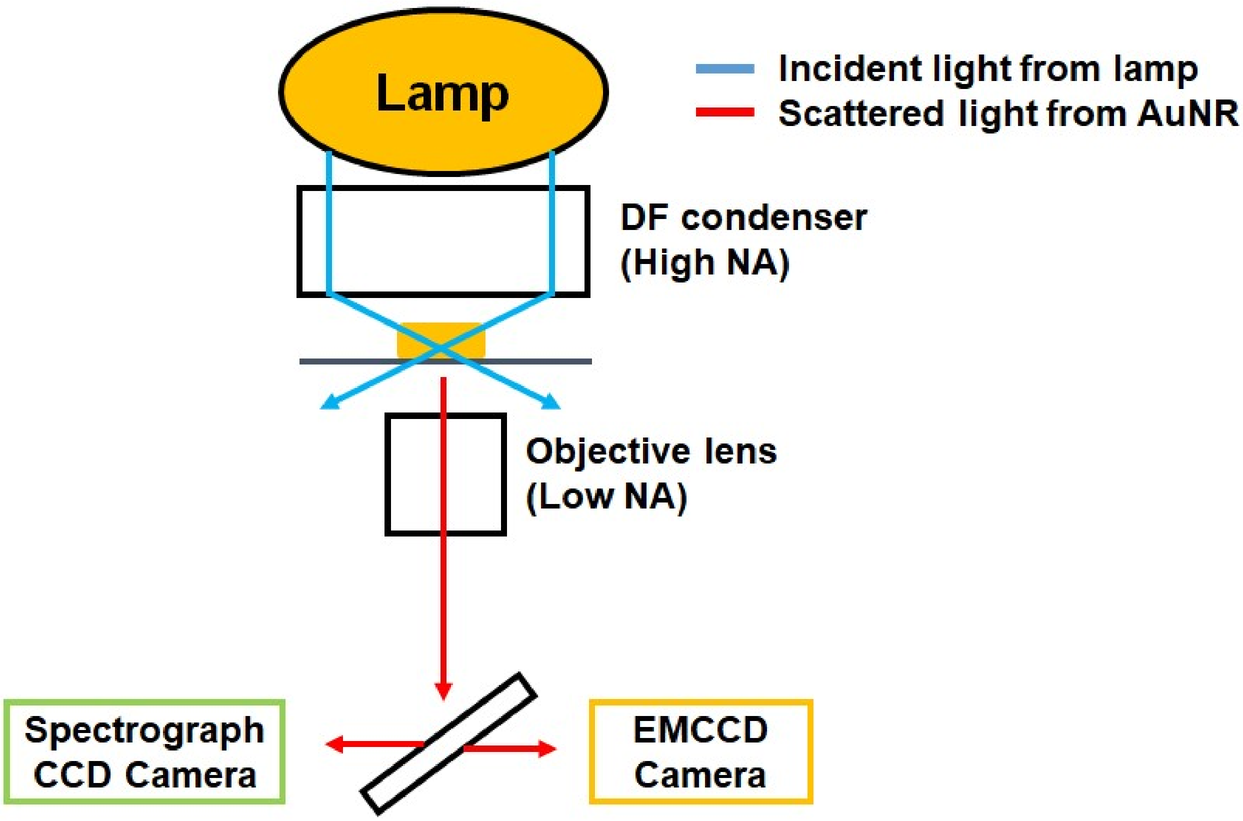

Fig. S4 Schematic to show the working principle of DF microscopy and spectroscopy

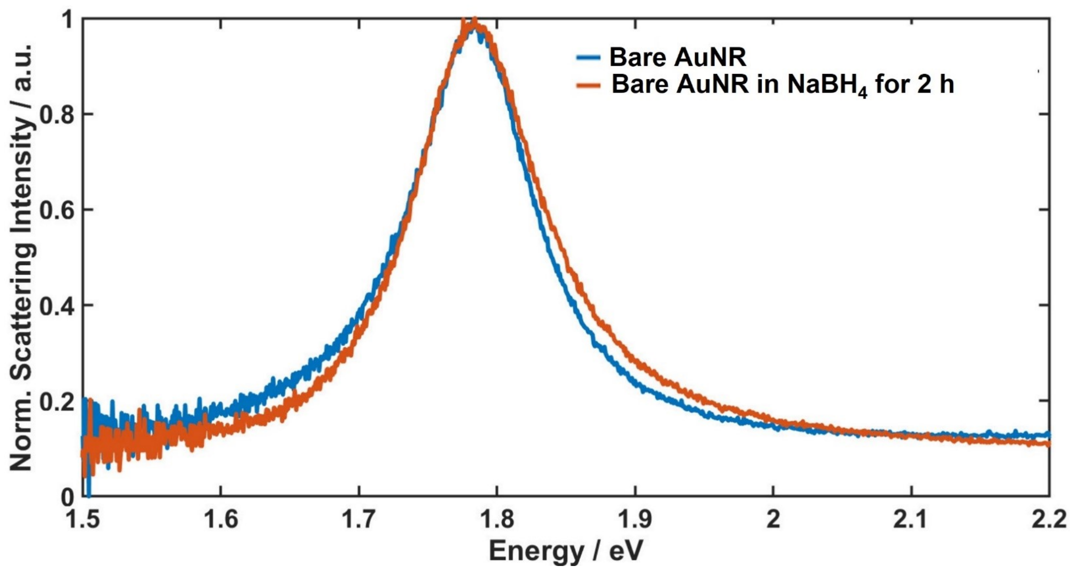

Fig. S5 Single particle scattering spectra of a bare AuNR before and after immersing it in $NaBH_4$ solution for 2 h without thiol molecules.

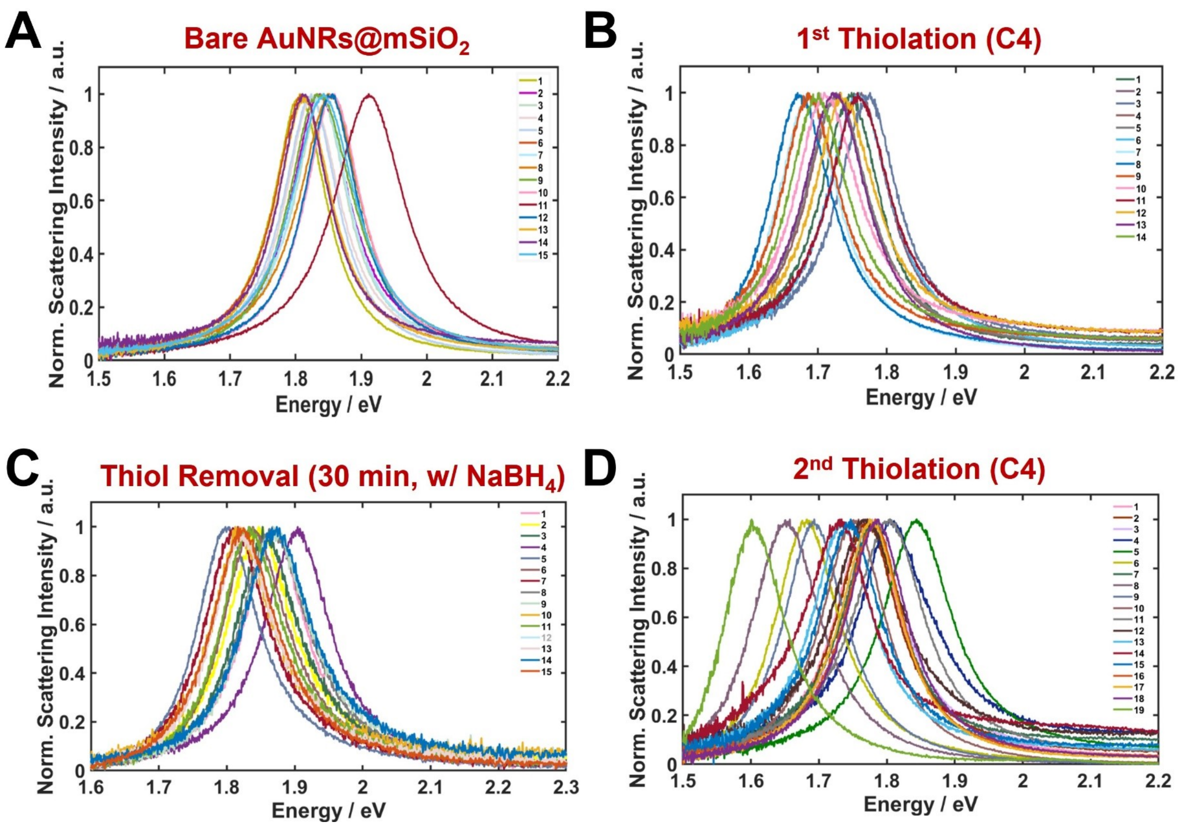

Fig. S6 (A) Single particle scattering spectra of bare AuNRs@mSiO_2. **(B)** Single particle scattering spectra of AuNRs@mSiO_2 after 1st thiolation with 1-butanethiol (C4). **(C)** Single particle scattering spectra of AuNRs@mSiO_2 after thiol removal using $NaBH_4$ solution. **(D)** Single particle scattering spectra of AuNRs@mSiO_2 after 2nd thiolation with 1-butanethiol (C4).

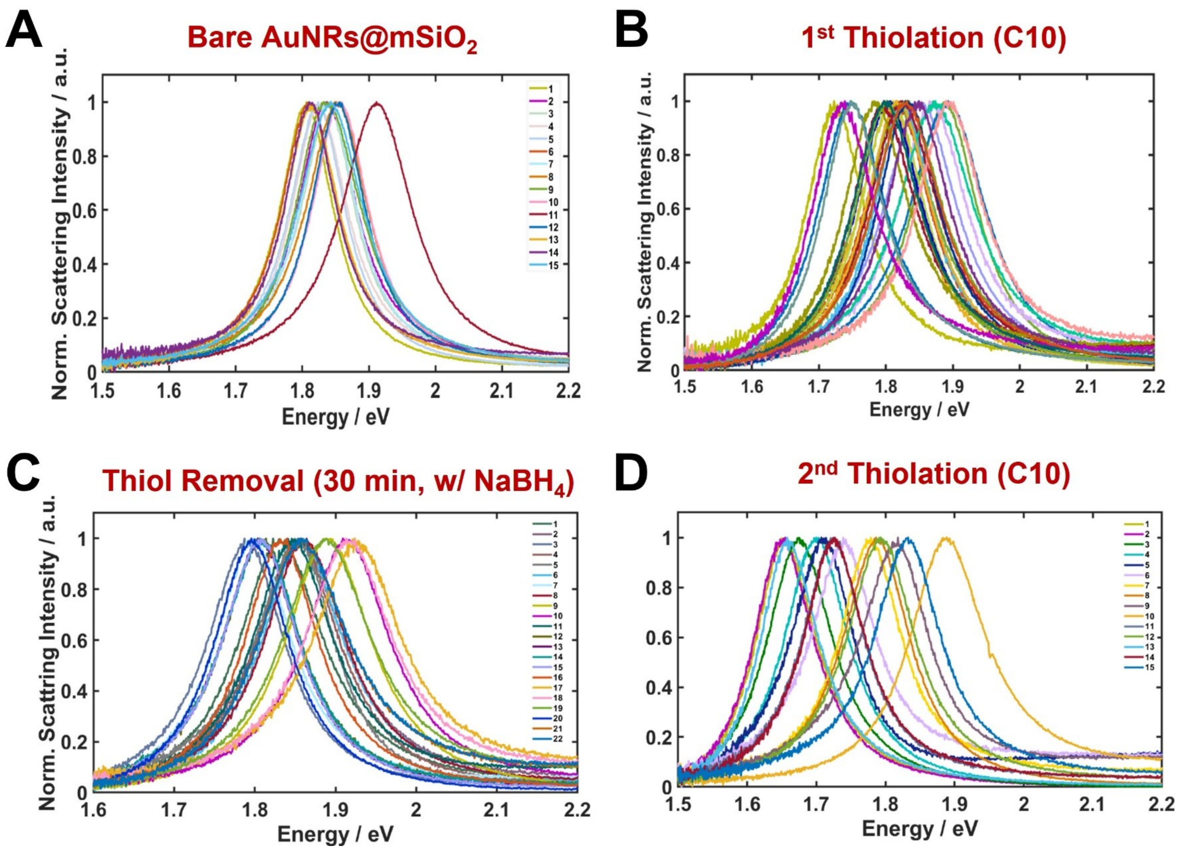

Fig. S7 (A) Single particle scattering spectra of bare AuNRs@mSiO_2. **(B)** Single particle scattering spectra of AuNRs@mSiO_2 after 1st thiolation with 1-decanethiol (C10). **(C)** Single particle scattering spectra of AuNRs@mSiO_2 after thiol removal using $NaBH_4$ solution. **(D)** Single particle scattering spectra of AuNRs@mSiO_2 after 2nd thiolation with 1-decanethiol (C10).

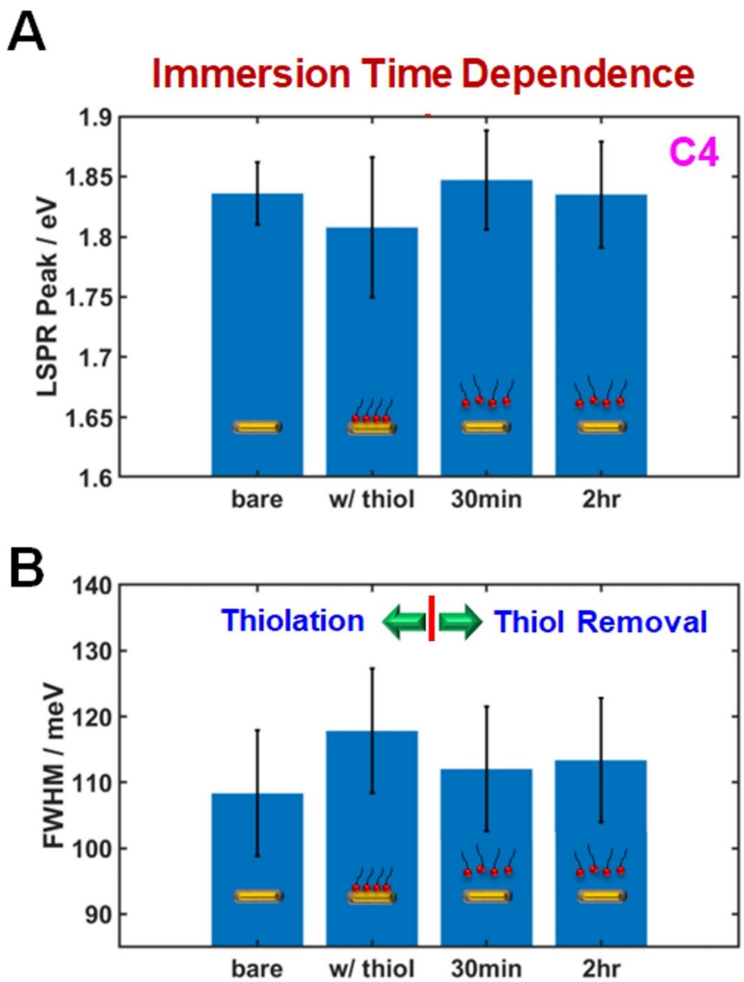

Fig. S8 (A) Effect of immersion time in $NaBH_4$ solution on the thiol removal from AuNRs@mSiO_2. Bar graphs showing changes in the LSPR peak wavelength before thiolation, after thiolation with 1-butanethiol, after immersion of the thiolated AuNRs@mSiO_2 in the solution for 30 min, and after immersion of the thiolated AuNRs@mSiO_2 in the solution for 2 h. **(B)** Bar graphs showing changes in the LSPR linewidth (or FWHM) before thiolation, after thiolation with 1-butanethiol, after immersion of the thiolated AuNRs@mSiO_2 in the solution for 30 min, and after immersion of the thiolated AuNRs@mSiO_2 in the solution for 2 h.