Electronic Supplementary Information

for

Influence of Oxygen Plasma Treatment on Structural and Spectral Changes in Silica-coated Gold Nanorods Studied Using Total Internal Reflection Microscopy and Spectroscopy

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Experimental Methods

Materials and Sample Preparation. CTAB-stabilized AuNRs (25 nm × 73 nm) and mesoporous silica-coated AuNRs (AuNRs@SiO$_2$, 30 nm × 90 nm) were purchased from Nanopartz (Loveland, CO, USA). The nanoparticle colloid solution was diluted with 18.2-MΩ pure water to the proper concentration and the diluted solution was sonicated for 15 min at room temperature to avoid the NR aggregation. The samples were then prepared by drop casting a diluted solution containing AuNRs (or AuNRs@SiO$_2$) on the pre-cleaned glass slide. Afterward, a 20 mm × 20 mm no. 1.5 coverslip (Corning, NY) was placed on the glass slide.

Structural Characterizations. After the samples (AuNRs@SiO$_2$) were treated with oxygen plasma, their structural characterizations were carried out using a scanning electron microscope (SEM, JSM6500F, JEOL, Japan). Then, we checked the structural changes of singe AuNRs@SiO$_2$ from SEM images and determined their length and diameter.

Oxygen Plasma Treatment. In this study, the oxygen plasma treatment was performed using a plasma cleaner (PDC-32G-2, Harrick plasma, U.S.A.). All oxygen plasma treatments were carried out with a maximum RF power of 18W at various plasma treatment times (0, 30, 180, 300, 600, 900, and 1200 s).

Total Internal Reflection Scattering (TIRS) Microscopy. The excitation of TIRS microscope was done using an inverted Nikon microscope (Nikon Eclipse Ti-2) with light-emitting diode (LED) lamps as an excitation source (Fig. S11). For TIRS microscopy, the beam from the LED

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 the DF and TIRS images of AuNRs. The collected images were analyzed by ImageJ and Matlab.

Total Internal Reflection Scattering Spectroscopy. Scattering spectra were acquired with a spectrometer (Andor, Kymer328i-A) and a CCD camera (Andor, Newton920) (Fig. S11). We mounted a relay lens system [a Newton lens system with two lenses (f = 7.5 cm)] between the microscope and the spectrometer system. When acquiring a spectrum of single AuNR (or AuNR@SiO$_2$), the relay lens system moved in a direction perpendicular to the optical axis by a translational stage. Here, instead of moving the sample stage, the image was moved by the objective lens, and only the scattered light from desired AuNR particles passed to the spectrometer. The light scattered by AuNRs was dispersed by a grating (300 l/mm; 700-nm center wavelength) and detected by the CCD camera. To measure the background, a region without any particles was selected. The experimental scattering spectra were fitted to a Lorentzian function to measure the LSPR linewidth and resonant wavelength.

Simulation of Scattering Patterns of AuNRs

We used the simulation program developed by Enderlein and Böhmer[1]. The program is designed to calculate the characteristic intensity distribution from an emitter with three perpendicular emission dipoles of different emission strength. It has been widely used to

determine the spatial orientation of single dye molecules[1, 2]. The simulation program is a special Matlab based utility with a graphics user interface (GUI) for easy calculation. This program allows us to calculate exactly the defocused (or focused) images of single molecules. For using the GUI, one should download the files from the website (https://www.uni-goettingen.de/de/imaging+of+single+molecules/512319.html).

The parmeters that can be input are : the numerical aperture of the objective lens, magnification of imaging, extent of defocusing (or defocusing distance in micrometers), κ and R. For defining the emission strength ratios of the three independent dipoles (Fig. S14), we input the parameter κ and R into the program. The ratio κ defines the ratio of the emission strength of the b- to c- dipole (transverse dipoles, Fig. S14) as shown below.

$$I_b/I_c = (1-\kappa)/(1+\kappa) \quad \text{(Eq. 1)}$$

In this study the emission strength of the b- dipole is assumed to be same as that of the c- dipole. In addition, the ratio R defines the emission strength of the a- dipole (or longitudinal dipole) to the combined b- and c- dipoles (or transverse dipoles) as shown below.

$$R \times I_a + (1-R) \times (I_b + I_c) \quad \text{(Eq. 2)}$$

When R is 1, we only have the contribution from a- dipole (longitudinal dipole) to the image patterns. However, the other two transverse dipole (b- and c-) start to contribute to the image patterns with decreasing the ratio R. That is, lower R values indicate more contributions from the

two transverse dipoles. Therefore, we were able to calculate the scattering patterns of a AuNR core inside a silica shell by adjusting the important parameters.

References

1.   M. Böhmer and J. Enderlein, *Journal of the Optical Society of America B*, 2003, **20**, 554-559.
2.   M. A. Lieb, J. M. Zavislan and L. Novotny, *Journal of the Optical Society of America B*, 2004, **21**, 1210-1215.

Supplementary Figures
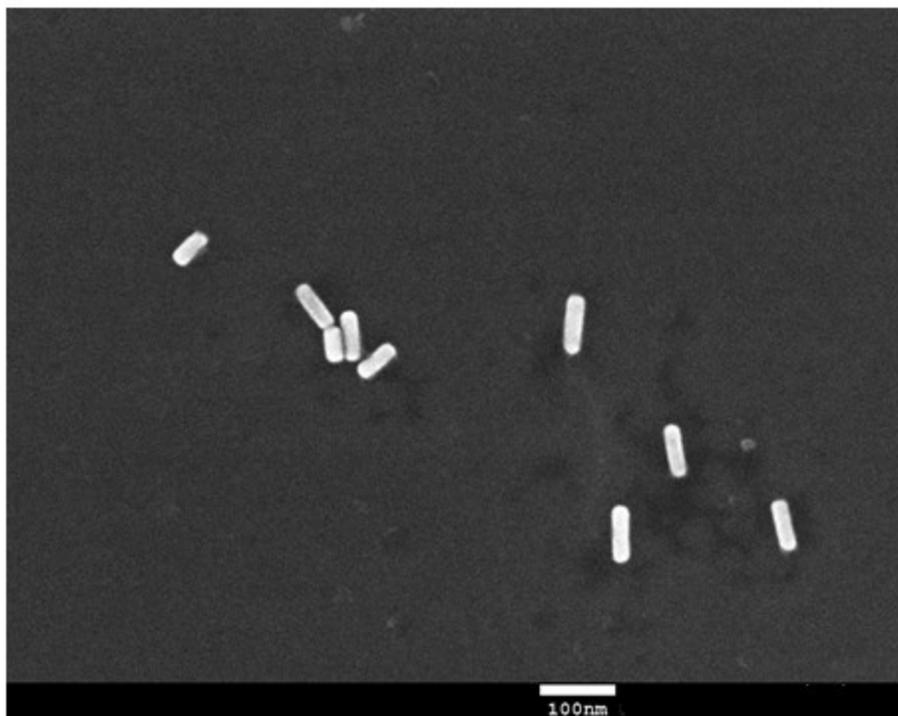
Fig. S1 SEM image of AuNRs (25 nm × 75 nm on average) used in this study
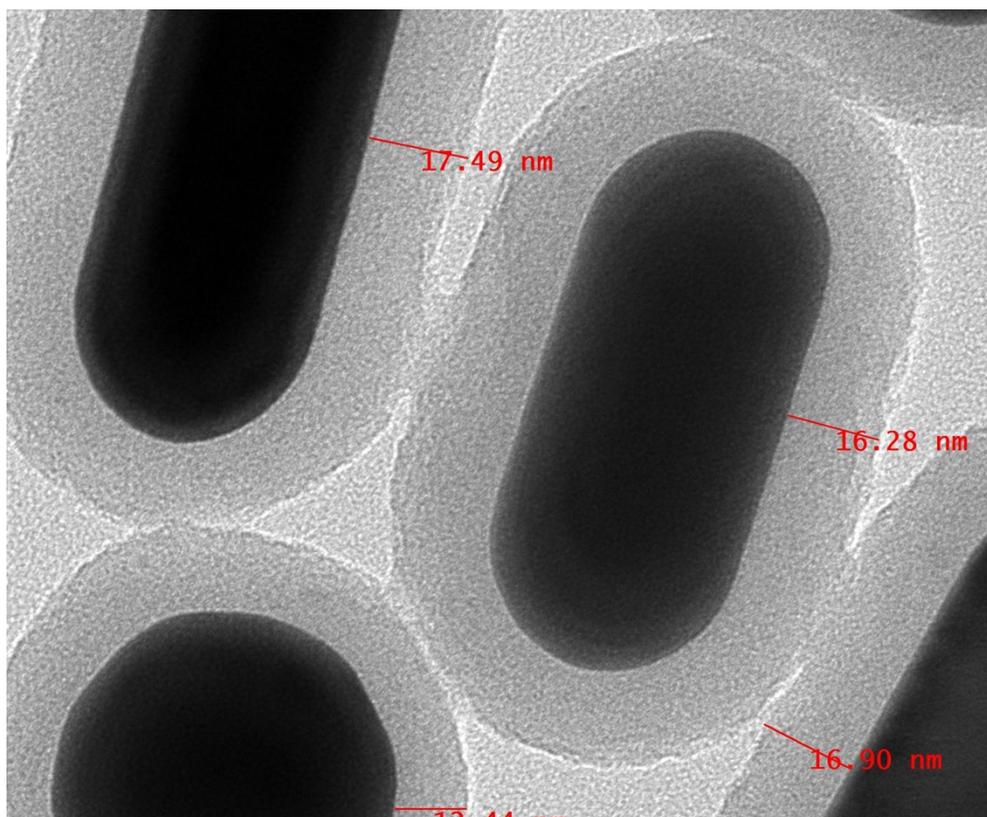
Fig. S2 TEM image of AuNRs@SiO₂. The thickness of silica coating is measured to be about ~17 nm.

UV-Vis Absorption Spectrum
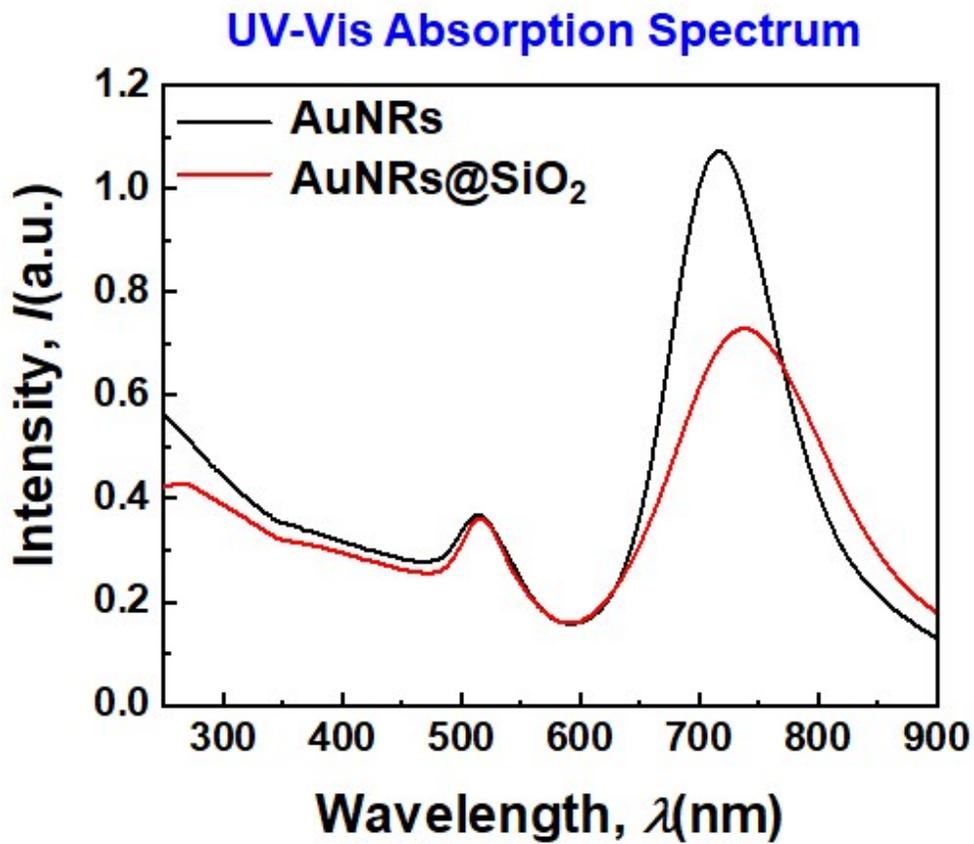
Fig. S3 Overlaid UV–Vis extinction spectra of AuNRs (black-curve) and AuNRs@SiO$_2$ (red-curve). Two distinct transverse and longitudinal LSPR peaks are observed for the AuNRs.
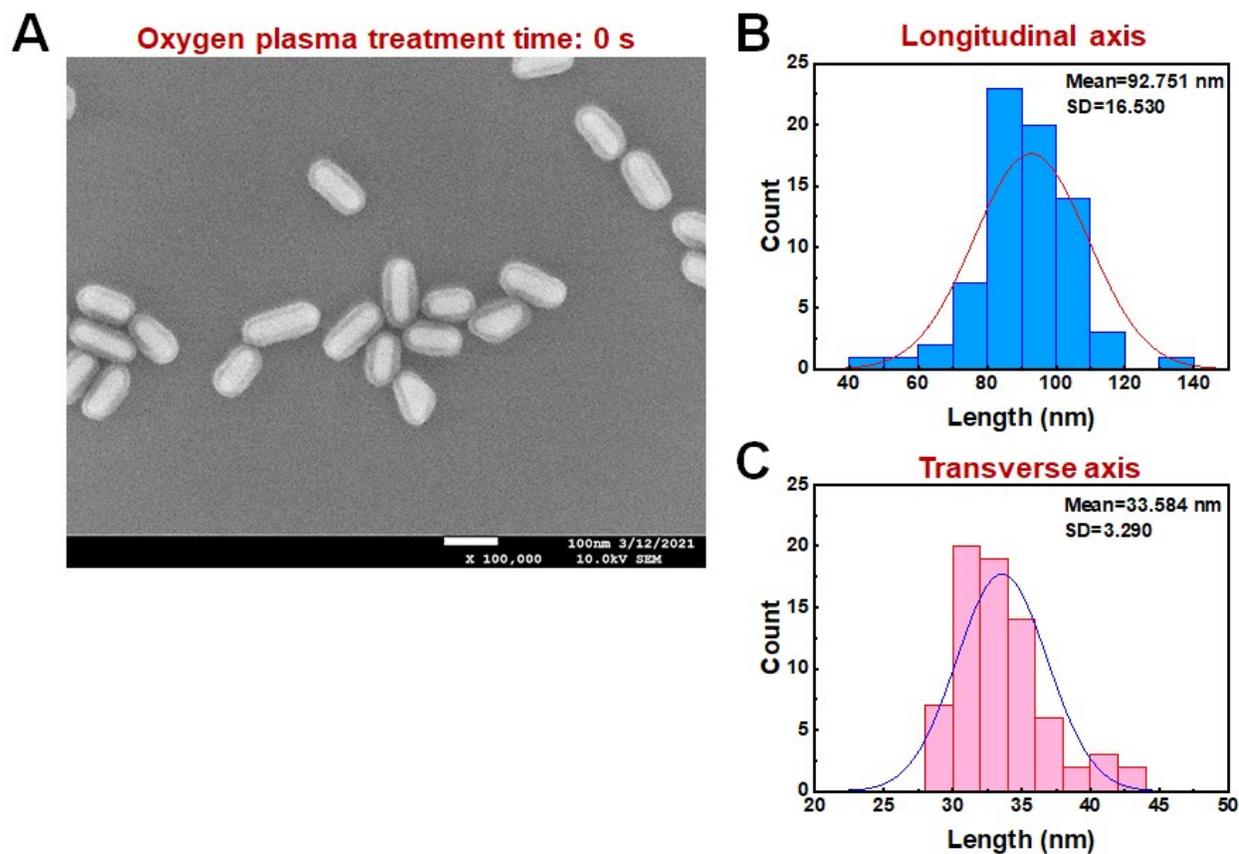
Fig. S4 (A) SEM image of AuNRs@SiO$_2$ before the oxygen plasma treatment (0 s). **(B, C)** Histograms of longitudinal axis (length, B) and transverse axis (width, C) of AuNRs inside the silica shell. The sizes of AuNRs@SiO$_2$ were determined by their SEM images in this study.
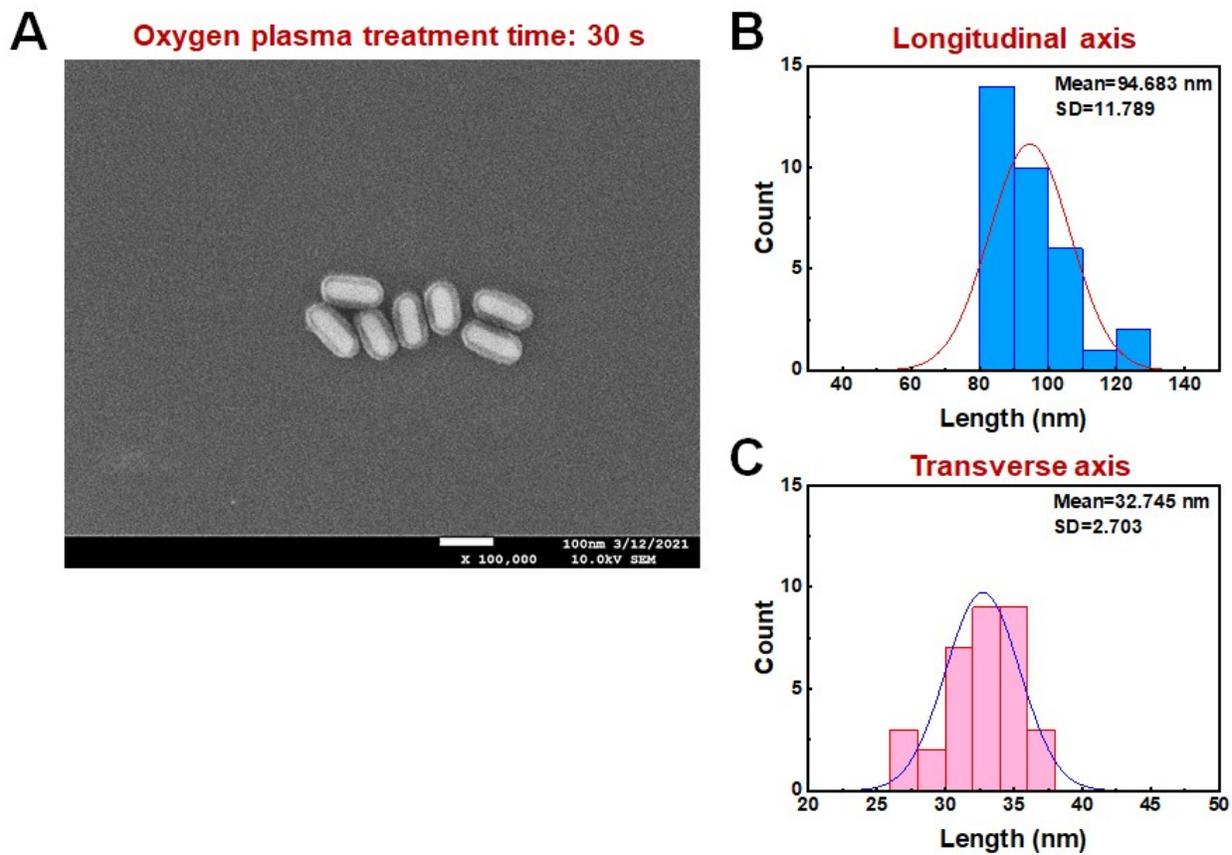
Fig. S5 (A) SEM image of AuNRs@SiO$_2$ after the oxygen plasma treatment (30 s). **(B, C)** Histograms of longitudinal axis (length, B) and transverse axis (width, C) of AuNRs inside the silica shell. The sizes of AuNRs@SiO$_2$ were determined by their SEM images in this study.
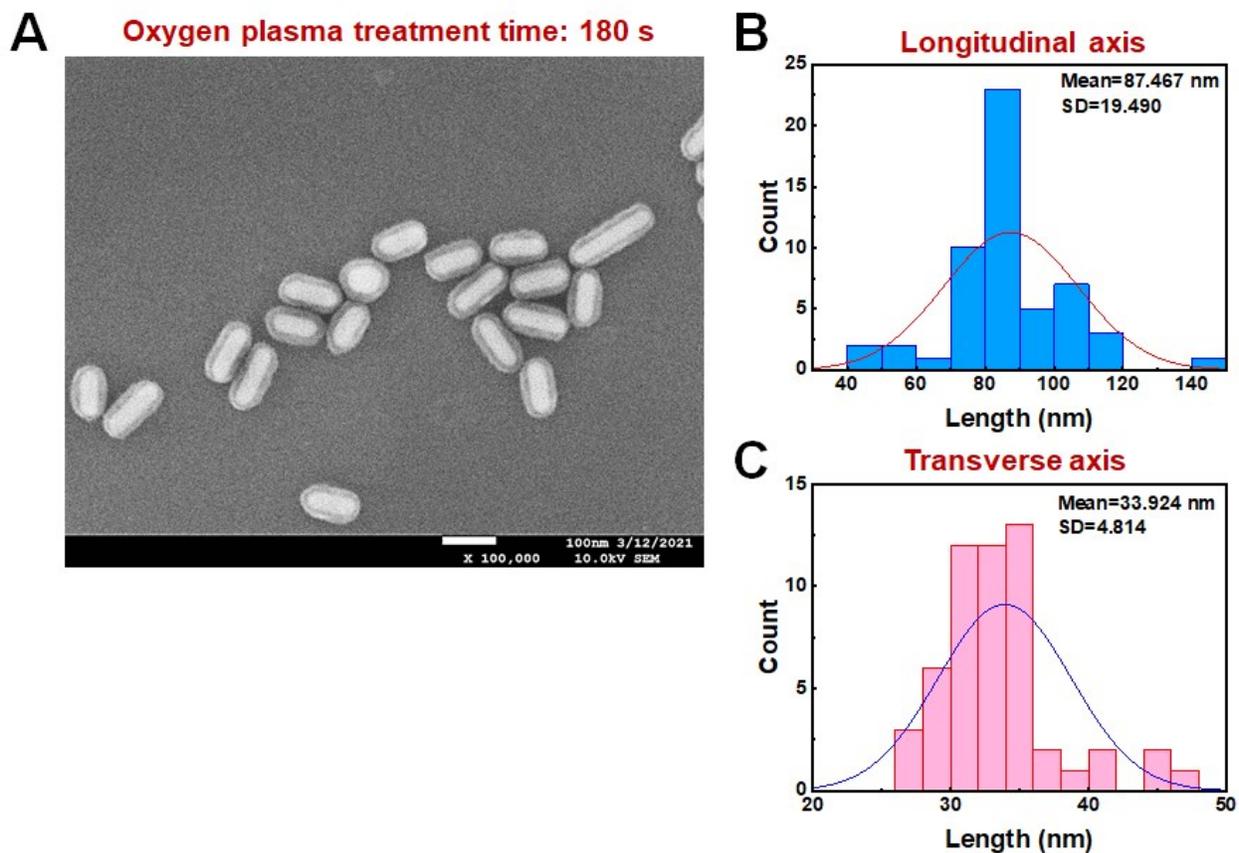
Fig. S6 (A) SEM image of AuNRs@SiO$_2$ after the oxygen plasma treatment (180 s). **(B, C)** Histograms of longitudinal axis (length, B) and transverse axis (width, C) of AuNRs inside the silica shell. The sizes of AuNRs@SiO$_2$ were determined by their SEM images in this study.
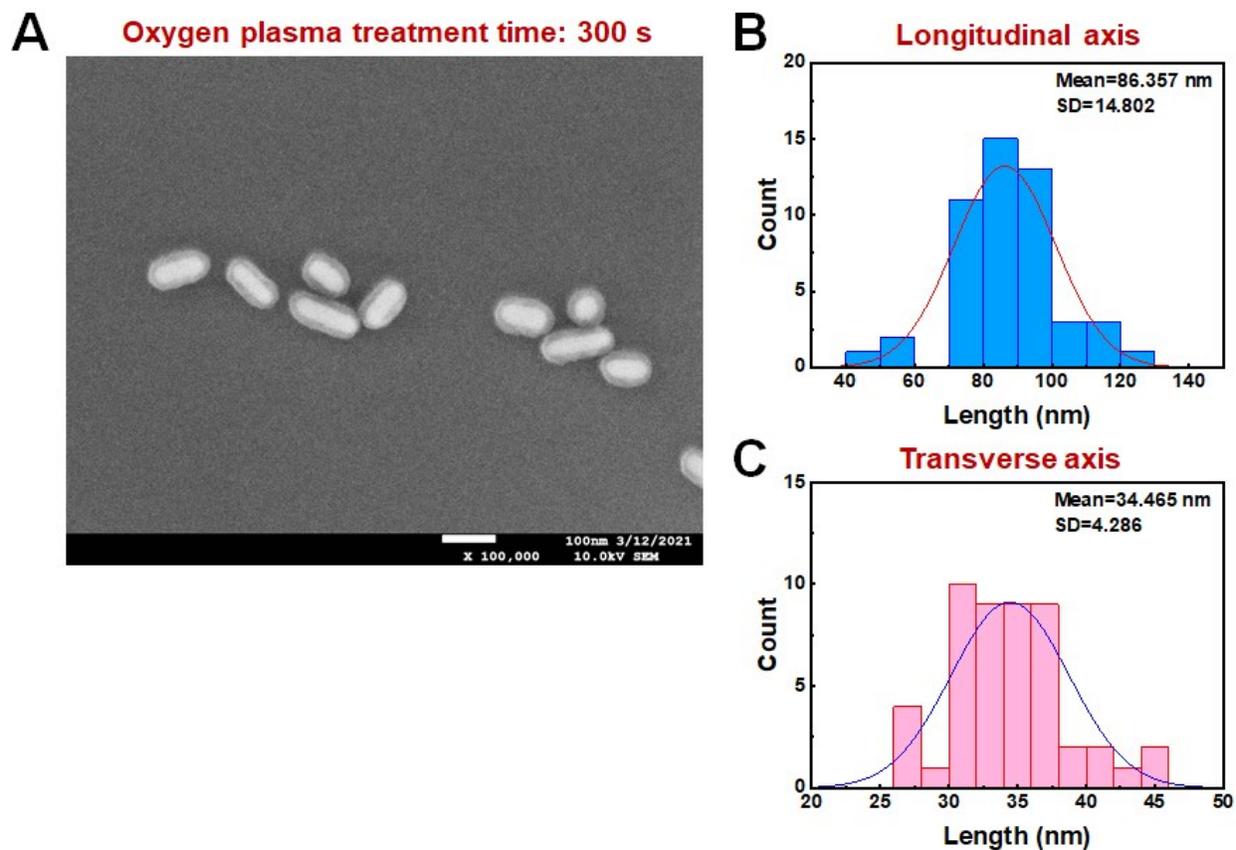
Fig. S7 (A) SEM image of AuNRs@SiO$_2$ after the oxygen plasma treatment (300 s). **(B, C)** Histograms of longitudinal axis (length, B) and transverse axis (width, C) of AuNRs inside the silica shell. The sizes of AuNRs@SiO$_2$ were determined by their SEM images in this study.
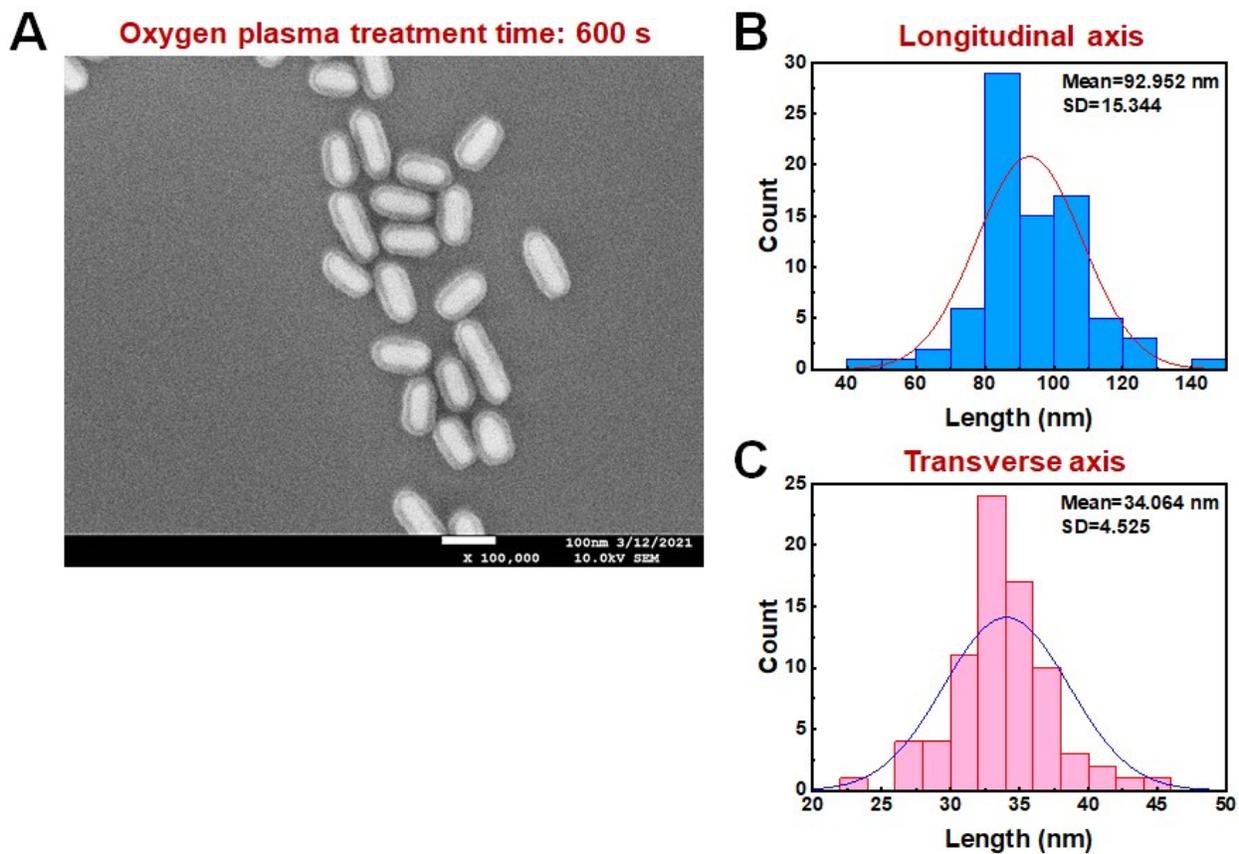
Fig. S8 (A) SEM image of AuNRs@SiO$_2$ after the oxygen plasma treatment (600 s). **(B, C)** Histograms of longitudinal axis (length, B) and transverse axis (width, C) of AuNRs inside the silica shell. The sizes of AuNRs@SiO$_2$ were determined by their SEM images in this study.
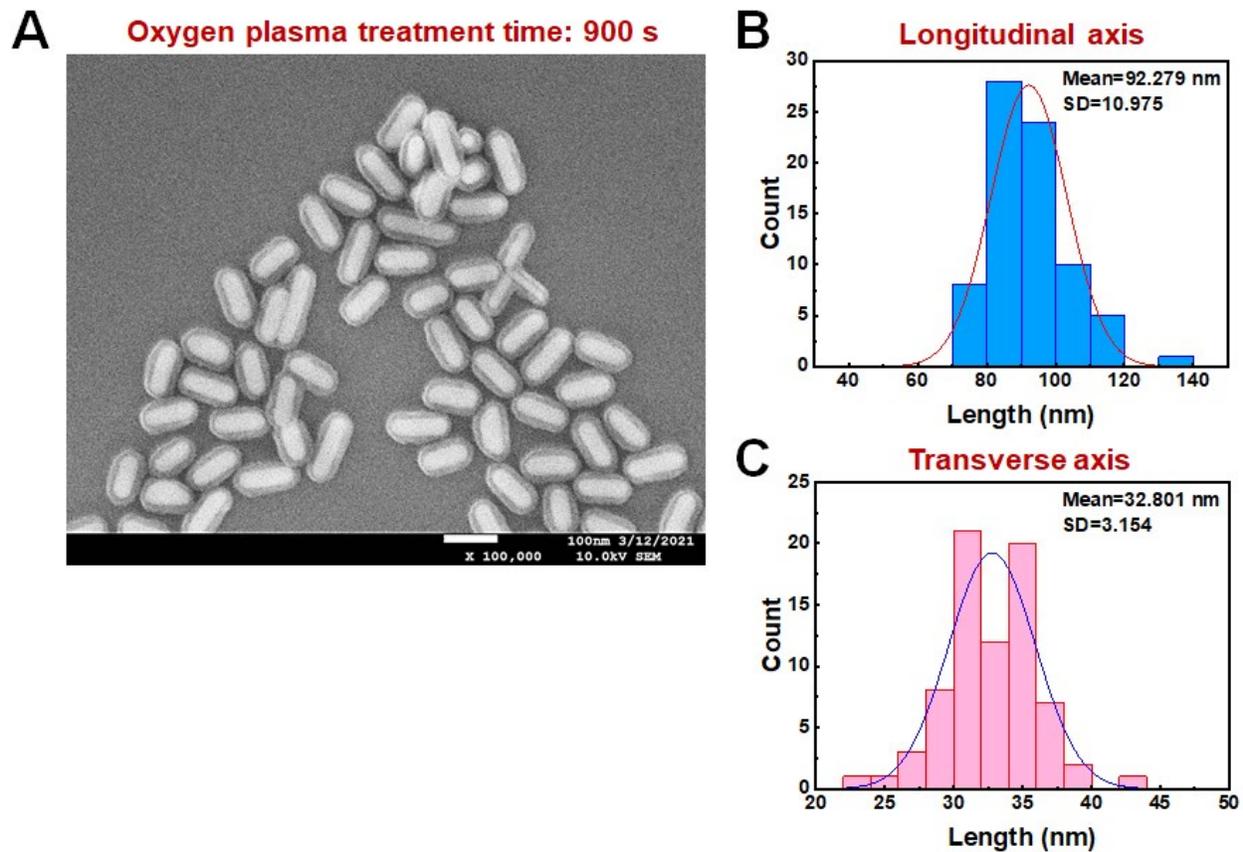
Fig. S9 (A) SEM image of AuNRs@SiO$_2$ after the oxygen plasma treatment (900 s). **(B, C)** Histograms of longitudinal axis (length, B) and transverse axis (width, C) of AuNRs inside the silica shell. The sizes of AuNRs@SiO$_2$ were determined by their SEM images in this study.
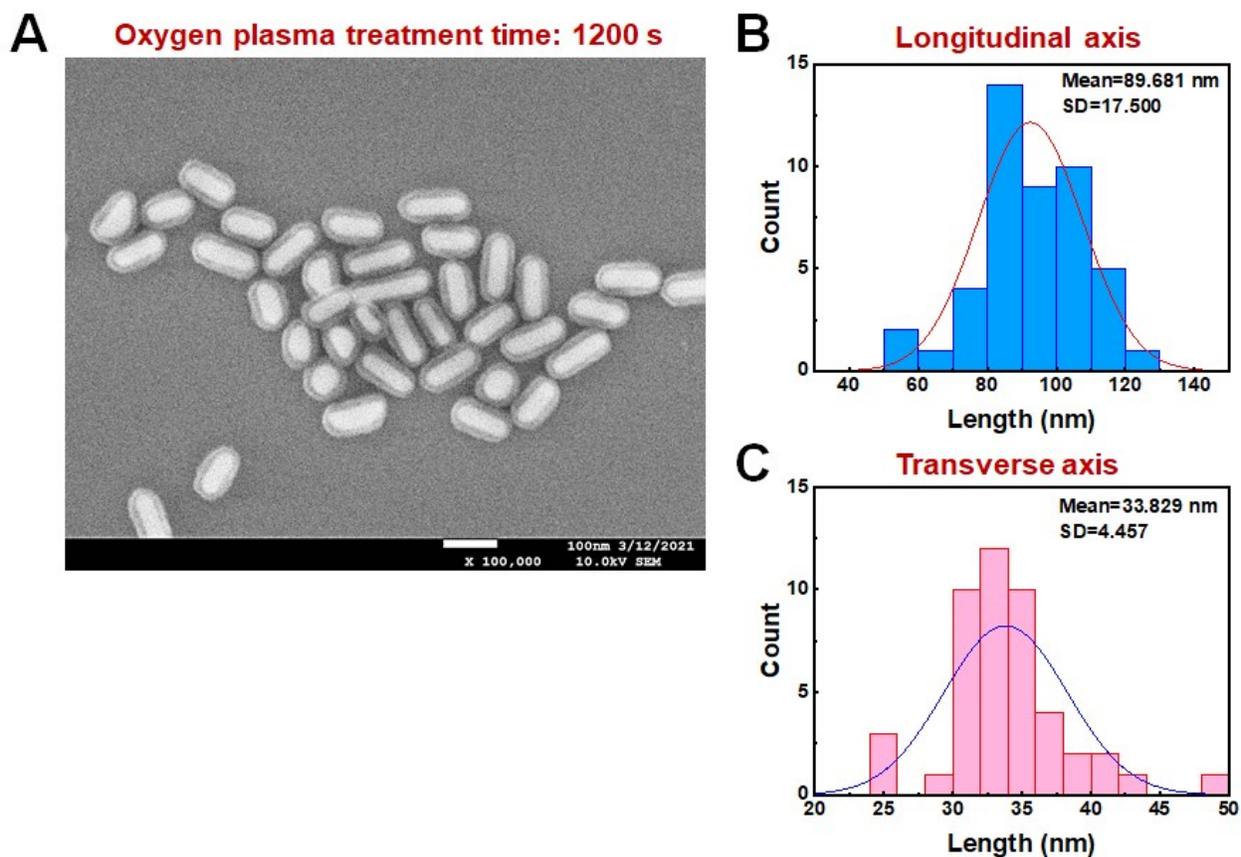
Fig. S10 (A) SEM image of AuNRs@SiO$_2$ after the oxygen plasma treatment (1200 s). **(B, C)** Histograms of longitudinal axis (length, B) and transverse axis (width, C) of AuNRs inside the silica shell. The sizes of AuNRs@SiO$_2$ were determined by their SEM images in this study.
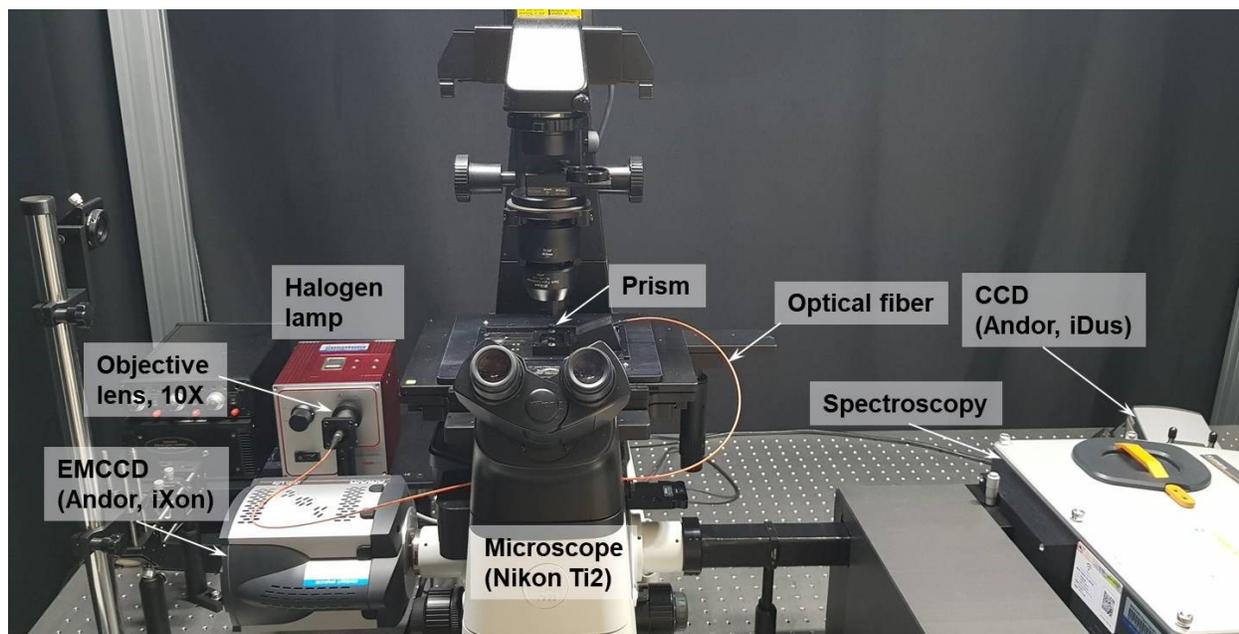
Fig. S11 A photograph showing the experimental setup for single particle TIRS microscopy and spectroscopy.
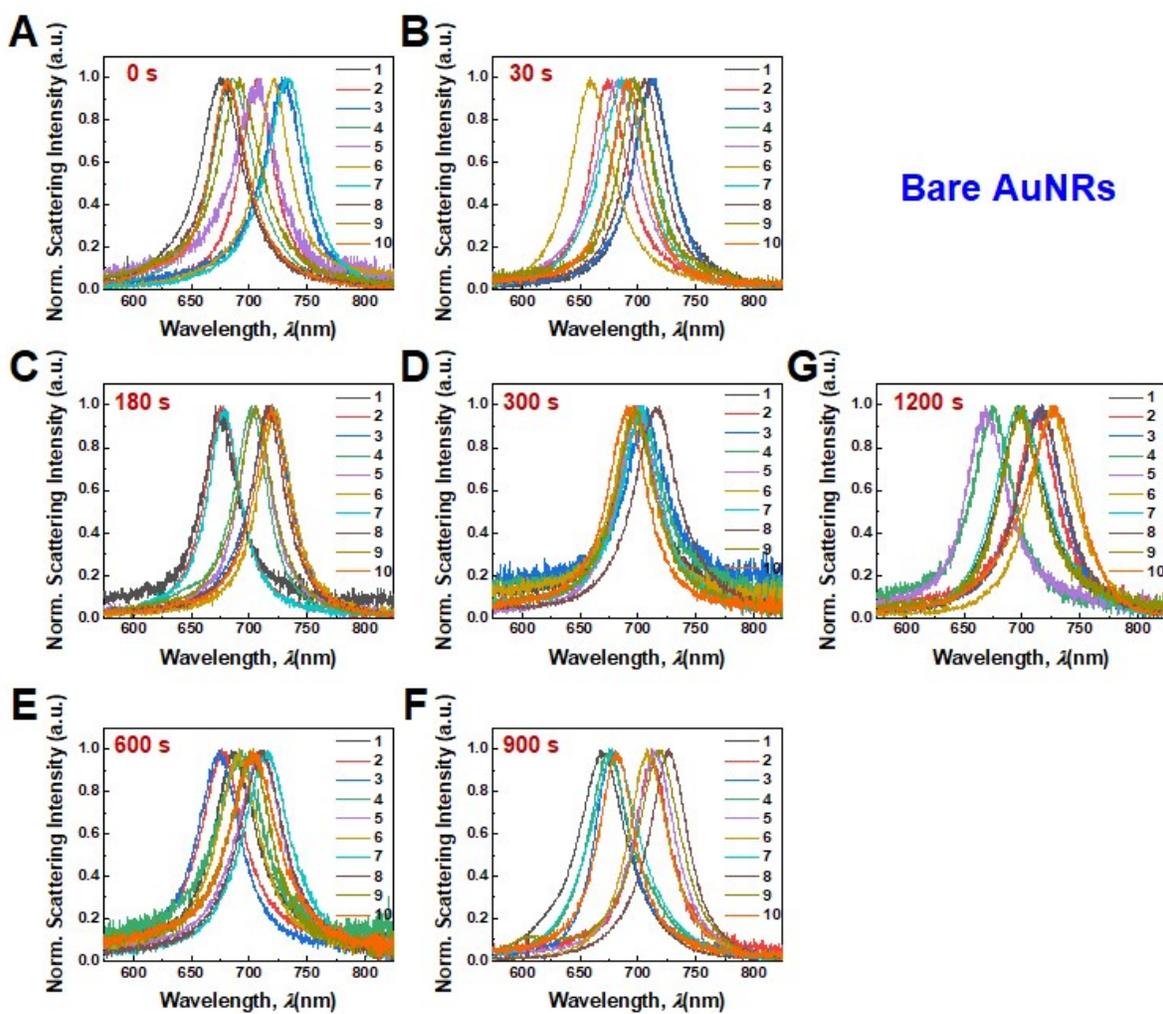
Fig. S12 Single particle scattering spectra of many bare AuNRs at various oxygen plasma treatment times of (A) 0 s, (B) 30 s, (C) 180 s, (D) 300 s, (E) 600 s, (F) 900 s, and (G) 1200 s.
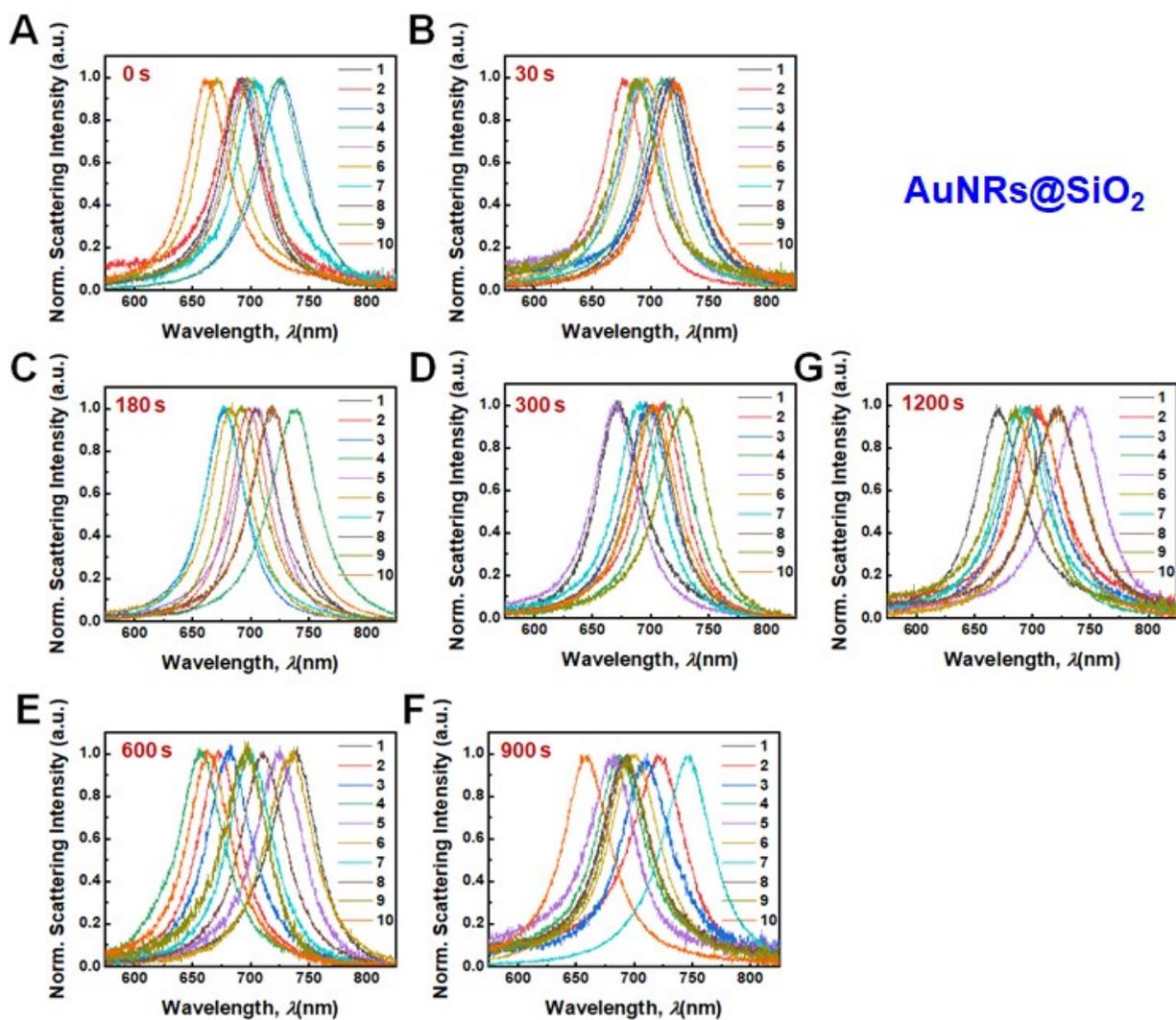
Fig. S13 Single particle scattering spectra of many AuNRs@SiO₂ at various oxygen plasma treatment times of (A) 0 s, (B) 30 s, (C) 180 s, (D) 300 s, (E) 600 s, (F) 900 s, and (G) 1200 s.
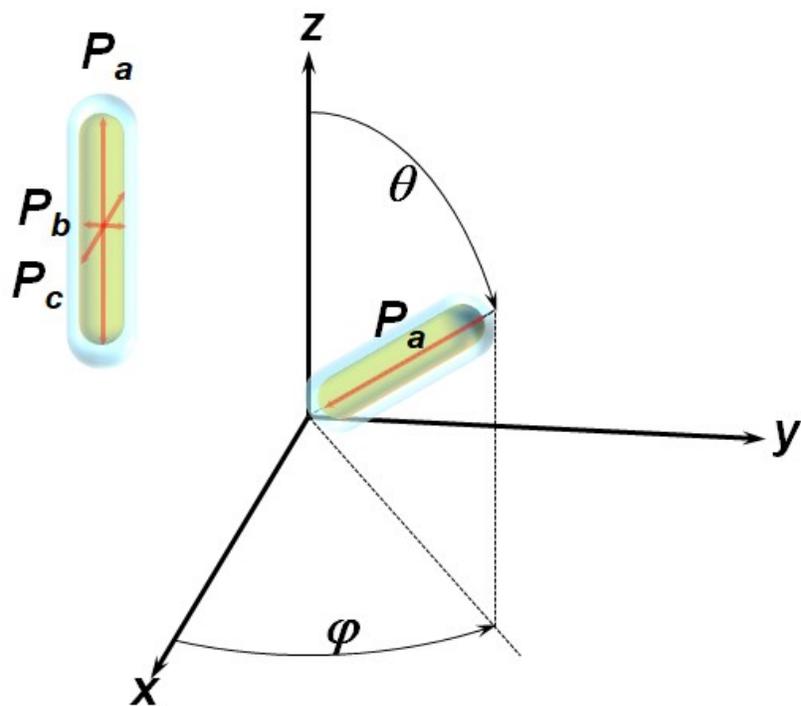
Fig. S14 Definition of azimuthal angle (φ) and polar angle (θ) of a AuNR@SiO$_2$ in 3D space.
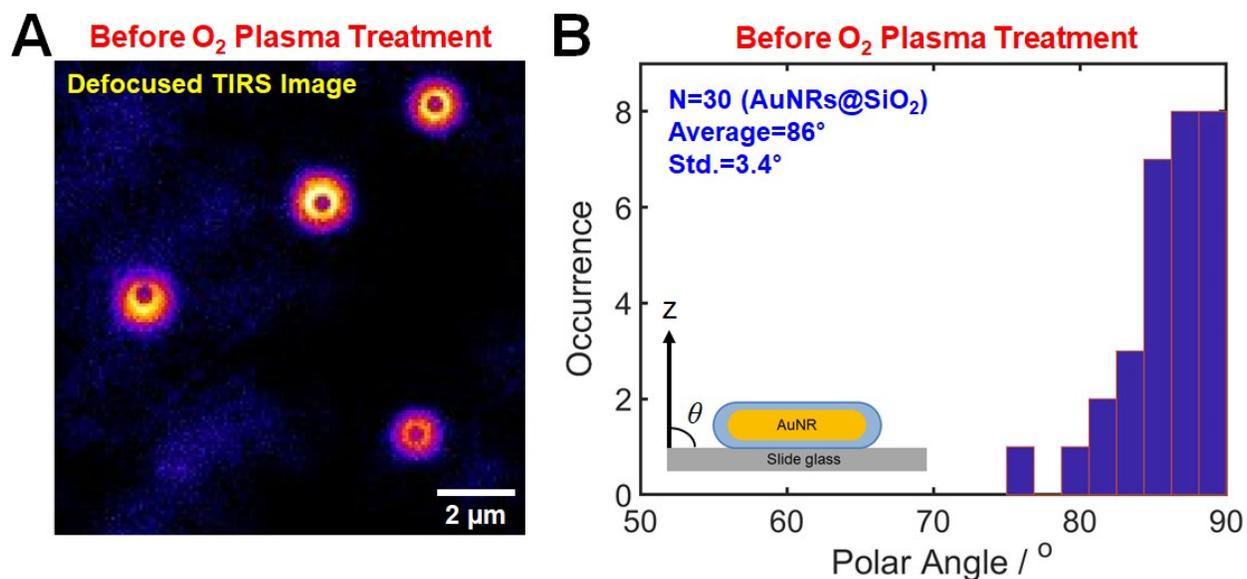
Fig. S15 (A) Defocused TIRS image of single AuNRs@SiO$_2$ before the oxygen plasma treatment. **(B)** Distribution of the 3D orientation of AuNR cores inside the silica shell before the treatment, which was determined from their characteristic defocused scattering patterns under TIRS microscopy.
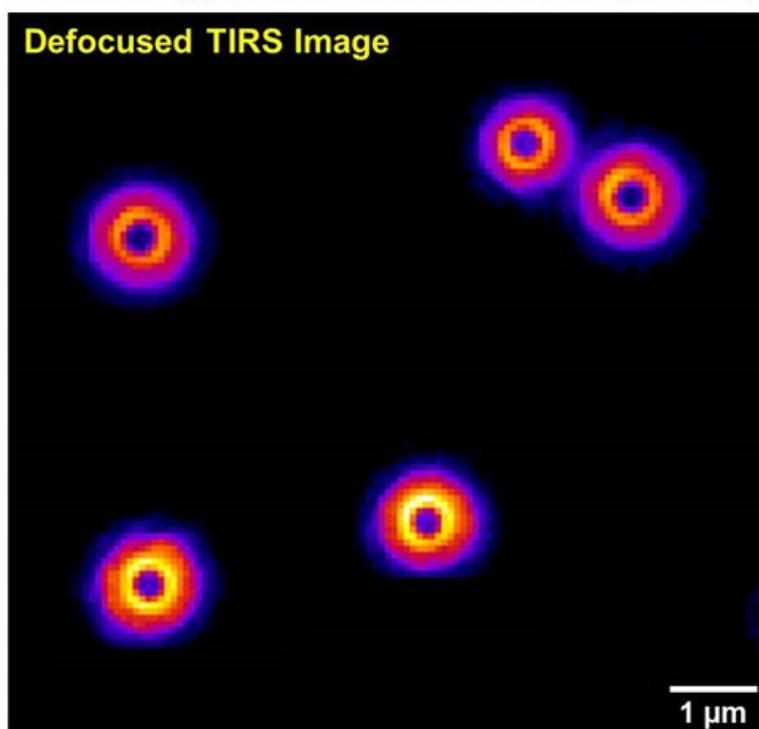
Fig. S16 Defocused TIRS image of single AuNRs@SiO$_2$ after the oxygen plasma treatment of 1200 s.