Electronic Supplemental Information

Ultra-High Sensitivity Detection of Gold Nanorods on a Blotting Membrane by Laser Induced Desorption/Ionization of Gold Ions

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Preparation of Gold Nanospheres:

The gold nanospheres were prepared by a stepwise seeding method in CTAC and CTAB solutions.[1] Seed particles were obtained in a CTAC solution at 5 °C. Soon after the preparation of the seed solutions, 300 µL of the solution was added to a growth solution comprising aqueous CTAB (10 mL, 80 mM) and tetrachloroaurate (1 mL, 1 mM). The growth reaction was then stirred for 10, 20, and 40 min for the 2nd, 3rd, and 4th steps, respectively.

Surface Modification of Gold Nanoparticles and Sample Preparation for Mass Measurements:

The gold nanorods and the nanospheres were centrifuged twice and dispersed in a solution of poly(styrene sulfonate) sodium salt (PSS, American Polymer Standards, Mw 9500, 2 mg·mL^{-1}) solutions to produce PSS-wrapped nanoparticles. The resulting mixtures were centrifuged and dispersed in water to remove excess PSS in solution and the nanoparticles were diluted to show the same absorbance (4.3×10^{-2}) at 355 nm, which was the excitation Laser wavelength. The concentrations of the PSS-wrapped gold nanoparticle solutions were evaluated by colorimetry with o-tolidine.[2] The absorbance gave concentrations of gold atoms and under these conditions, the concentrations of gold atoms were almost constant (10 µM) among the solutions.

Extinction spectra of the solutions were measured using a conventional spectrophotometer (V-670, JASCO, Japan). High-resolution scanning electron microscope (HR-SEM; SU-70, Hitachi High-tech, Japan) were used to evaluate the size distributions of gold nanoparticles.

Transmission electron microscopes (TEM, JEM-3010 and JEM-2100HCKM, JEOL, Japan), Scanning electron microscope (SEM, SU-70, Hitachi Hitech, Japan), and dynamic light scattering (Zetasizer Nano S, Mulvarn, UK) were also used to assess the particle sizes.
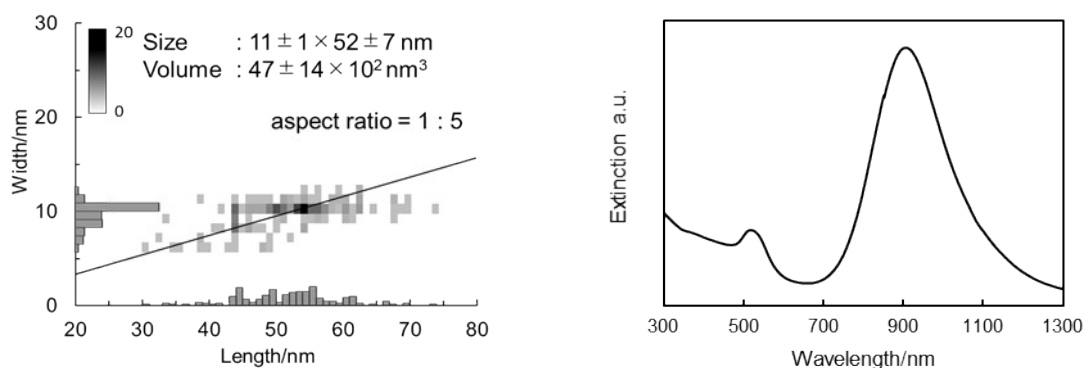

Fig. S1 Size distributions and extinction spectrum of gold nanorods wrapped with PSS. The distribution was obtained from HR-SEM images.
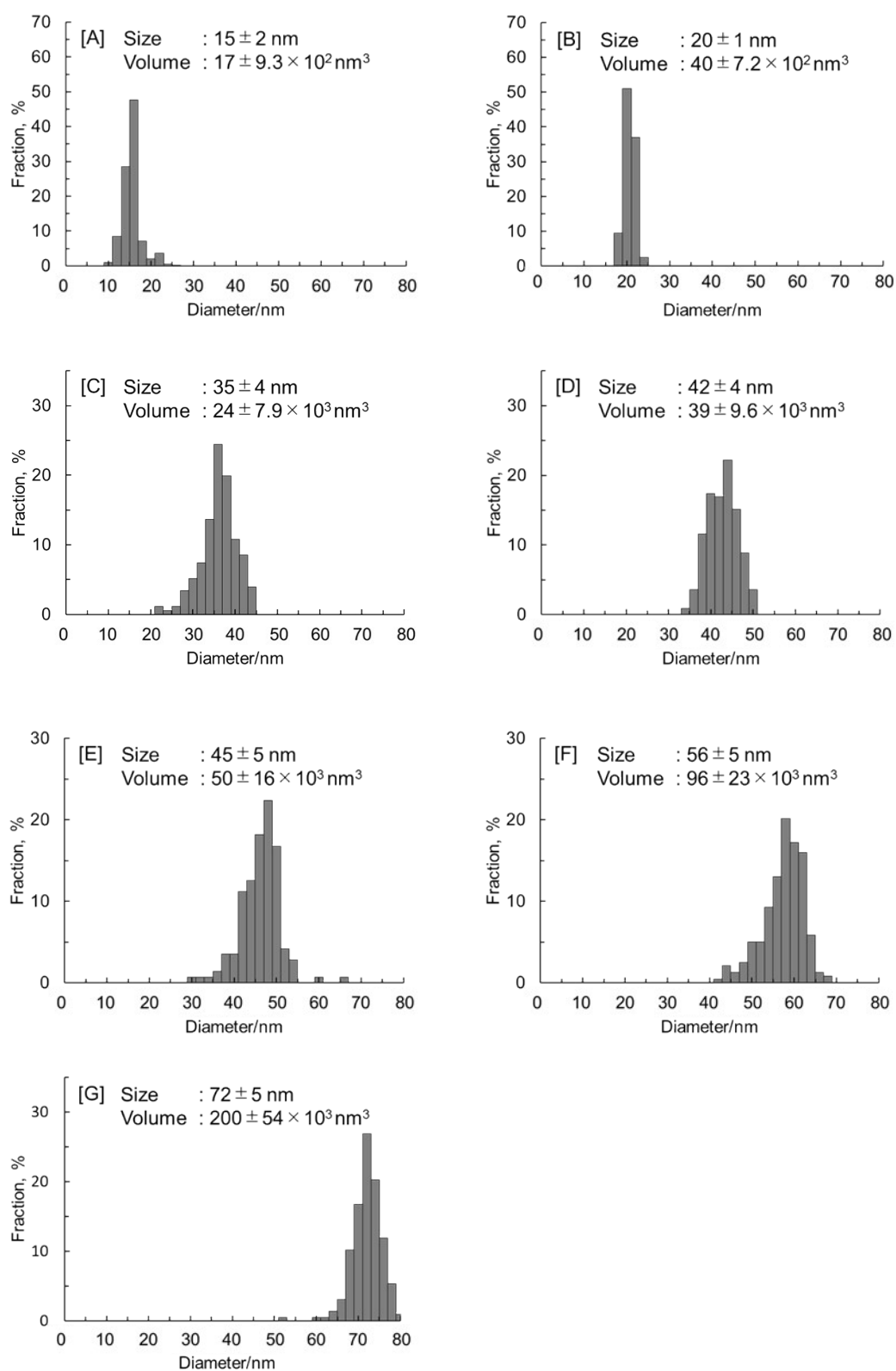
Fig. S2 Size distributions of the seven types of the gold nanospheres wrapped with PSS, as determined from HR-SEM images.
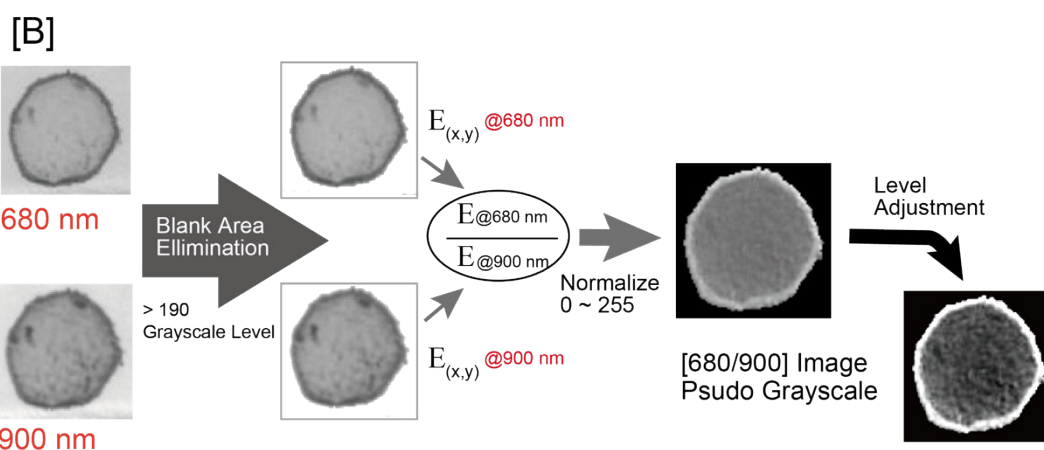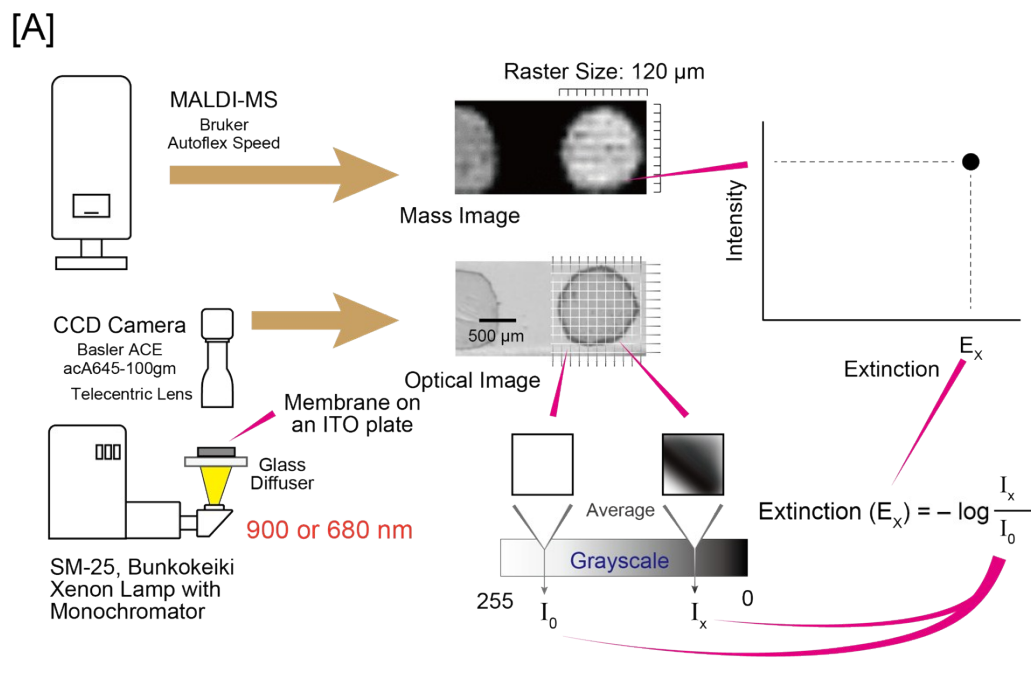
Fig. S3 Schematic illustration of the image processing. [A]: Preparation of plots of mass intensities against the extinction at the corresponding section. [B]: Image processing to obtain a [680/900] image.

[A] Plots of mass intensities against the extinction at the corresponding section: A sample membrane was put on a glass diffuser and illuminated by monochromatic light (680 and 900 nm) from a Xenon lamp. Images of the transmitted light were captured by a CCD camera (ace645-100gm, Basler, USA). An optical image was divided into 120×120 μm sections, and grayscale levels of the sections were converted to extinction. The grayscale level of the brightest section was assumed to be 100% transmittance (I_0), and grayscale levels of each section ($I_{(x, y)}$) was

calculated as an extinction ($E_{(x, y)}$) according to the following equation.

$$E_{(x,y)} = -\log\frac{I_{(x,y)}}{I_0} \qquad\qquad \rule{4cm}{0.4pt} \qquad (1)$$

Mass signals were obtained every 120 μm. Mass signal intensities were plotted against extinction of the corresponding sections.

[B] Image processing to obtain [680/900] ratio images: Two optical images were captured using 900 and 680 nm light. To exclude blank areas, where nanorods did not exist, we eliminated areas where the grayscale levels were larger than 190 from the images. This was necessary for the image processing. The grayscale levels of each pixel in the images were converted to extinctions using the same procedures shown as equation (1). The ratios of extinctions at 680 and 900 nm ([680/900]) were determined for each pixel. The ratios were normalized from 0 to 255, and the grayscale level was adjusted to show the distribution of the [680/900] ratio inside the coffee ring.
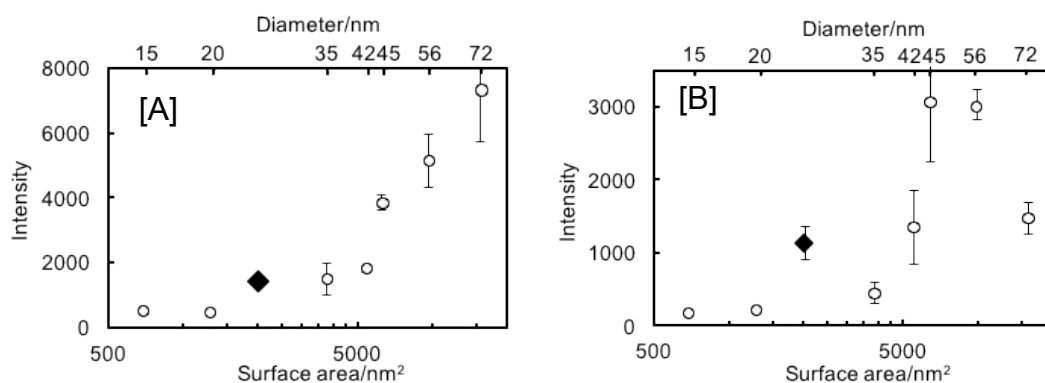

Fig. S4 Mass signal intensities plotted against the surface areas of gold nanoparticles cast on a blotting membrane [A] and a liver tissue section [B]. Open circles: signal intensities obtained from the gold nanospheres (upper x-axis indicates the diameters of the nanospheres), Filled diamond: mass signals obtained from gold nanorods. The gold nanoparticle solutions (10 μM (gold atoms)) were cast on a blotting

membrane. This figure was prepared from the identical data shown in Fig. 3.
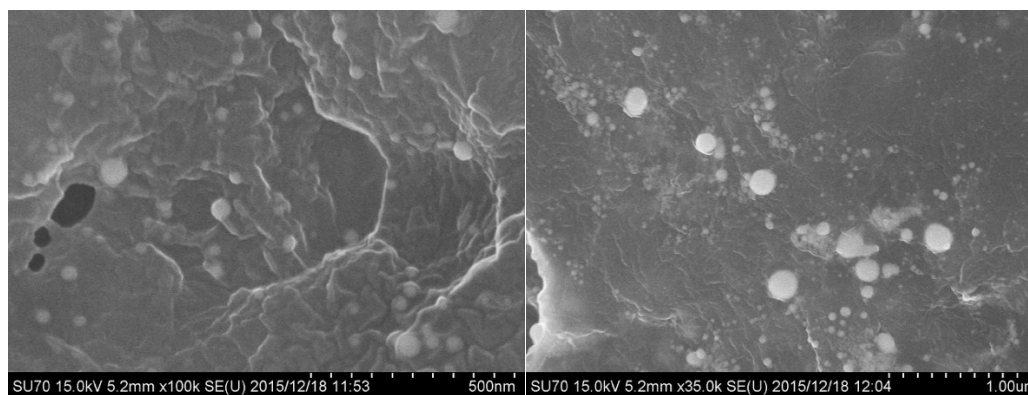

Fig. S5 HR-SEM images of the Laser irradiated membranes. Bright spheres indicate gold nanoparticles that were transformed from gold nanorods.
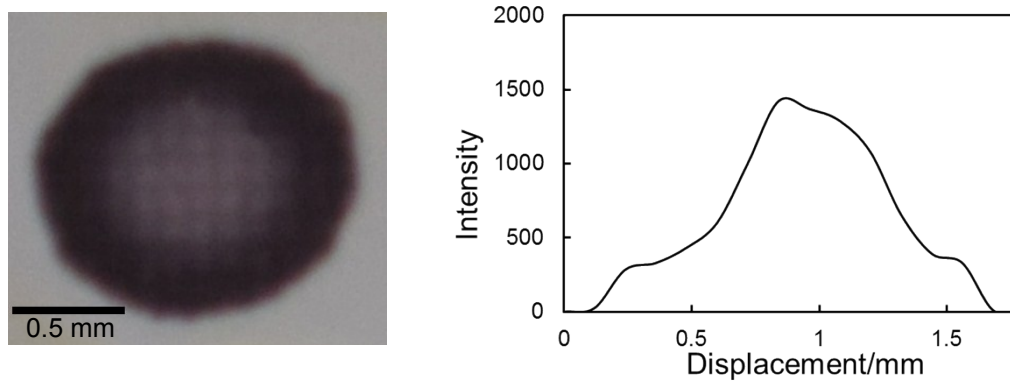

Fig. S6 Optical image of a nanorod cast area of a blotting membrane and a mass signal profile obtained at the line shown in the optical image. A nanorod solution (10 µM, 1.5 µL) was cast on the area and occasionally a thicker coffee ring was obtained. The mass signal profile indicates that the mass signal from the coffee ring area was small. Aggregation of nanorods in the coffee ring area suppressed the LDI of gold ions.
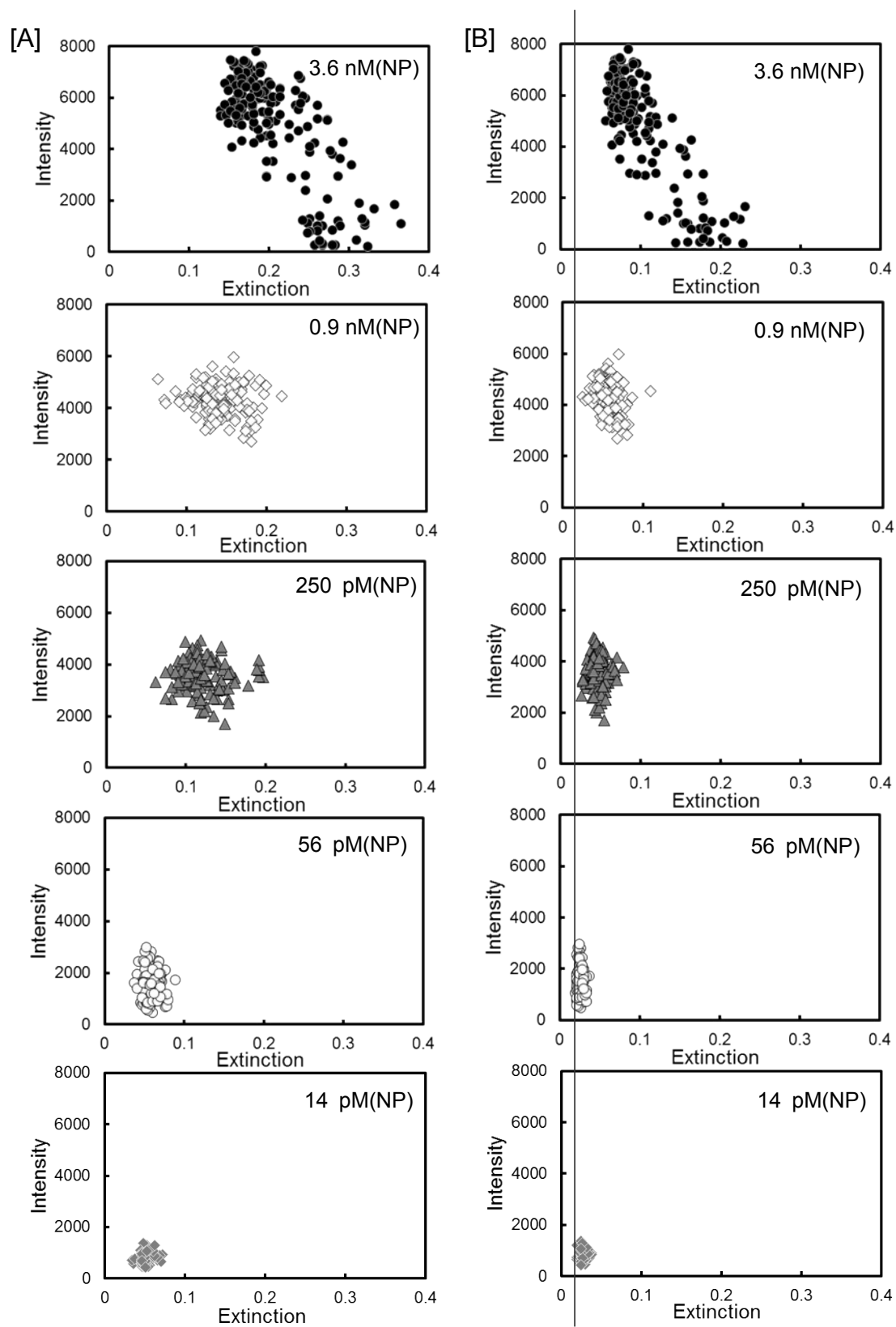
Fig. S7 Mass intensities plotted against the extinctions evaluated at 900 nm [A] and 680 nm [B] at the corresponding spots of the mass measurements.

Fig. S8 Optical image of the membrane on which gold nanorods were cast. The image was obtained using light at 680 nm. The membrane was identical to that of Fig. 4 in the main text.
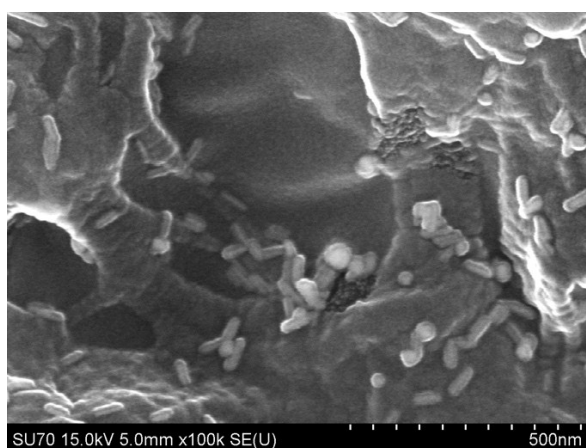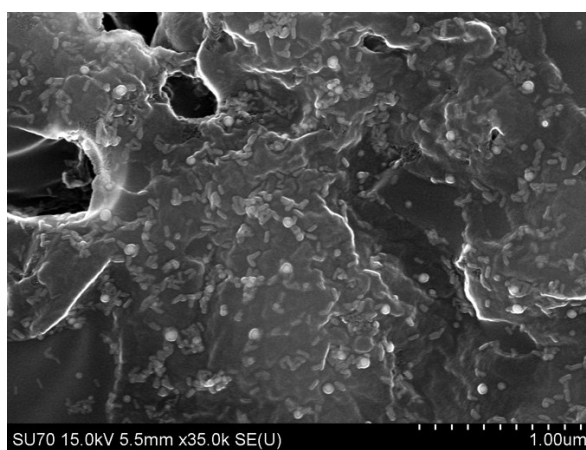

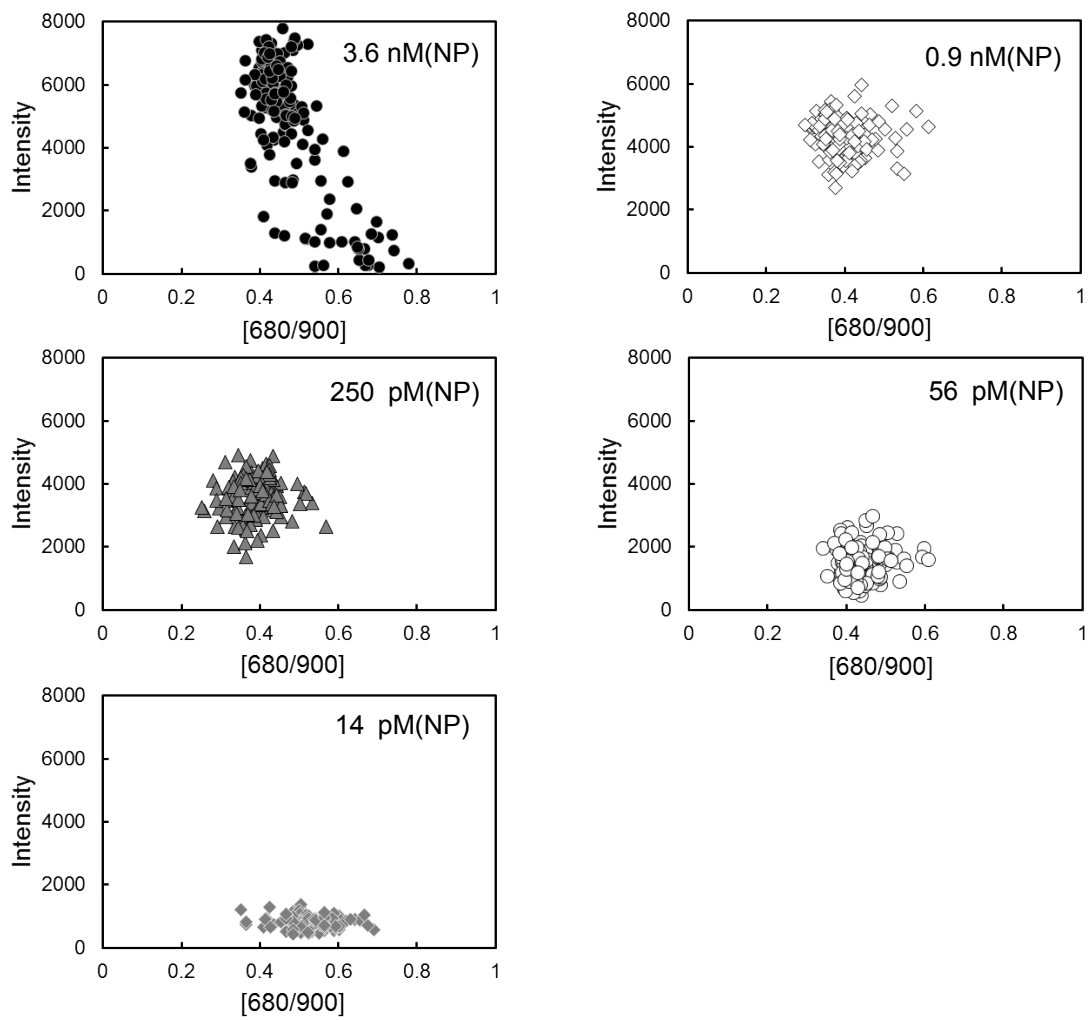Fig. S9 HR-SEM images of the nanorod aggregates in the coffee ring area.

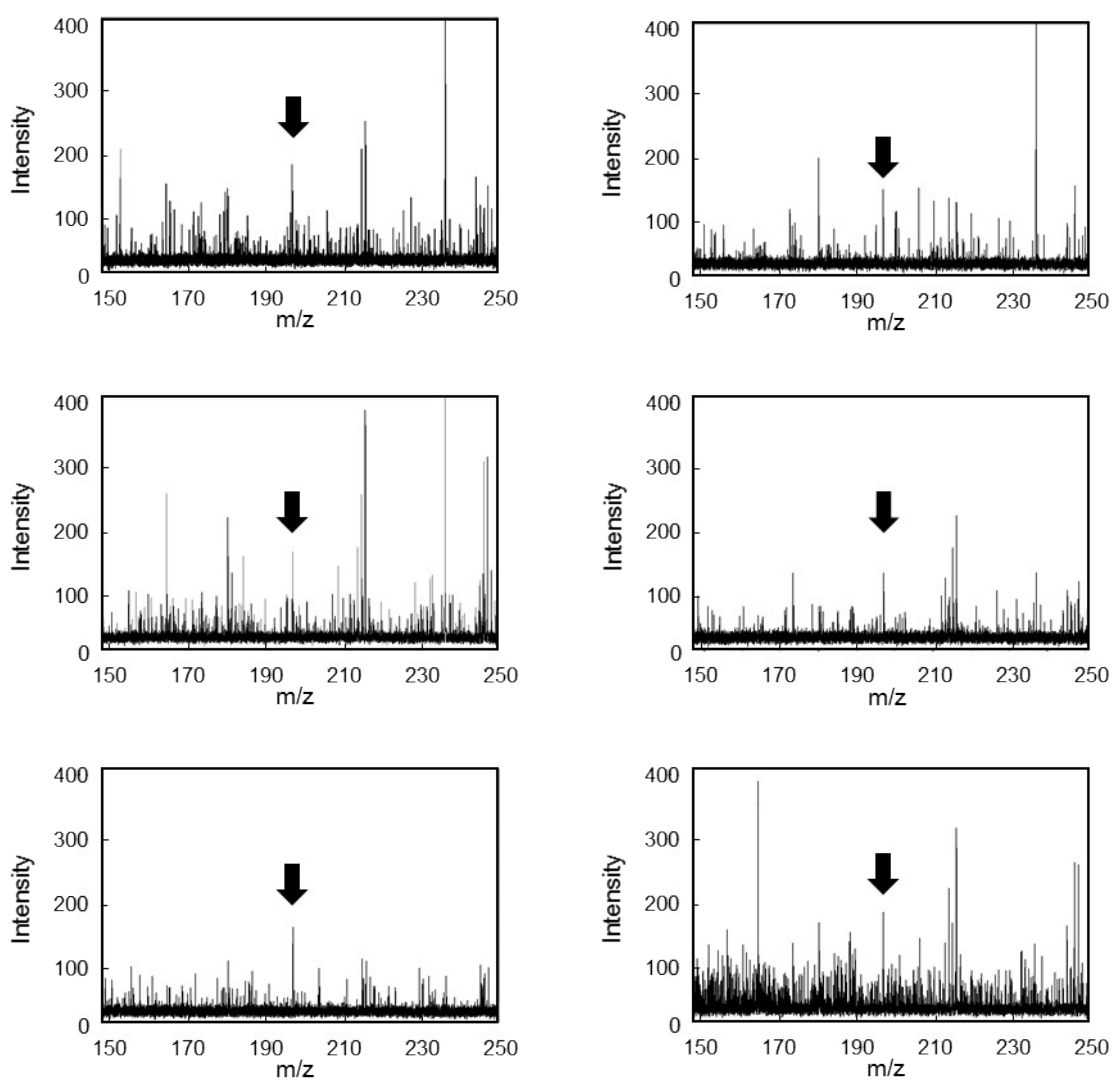Fig. S10 Mass signal intensities plotted against the ratio of extinctions at 680 and 900 nm [680/900].

Fig. S11 Mass spectra where the 18 fM(NP) of nanorod solution was cast.

References

1. Y. Inoue, Y. Tsutamoto, D. Muko, K. Nanamura, T. Sawada and Y. Niidome, *Anal. Sci.*, 2016, **32**, 875-880.

2. W. S. Clabaugh, *J. Research Natl. Bur. Standards*, 1946, **36**, 119.