

Supplementary Material (ESI) for Analyst

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## Use of thermally annealed multilayer gold nanoparticle films in combination analysis of localized surface plasmon resonance sensing and MALDI mass spectrometry

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The quality of these structures as well as the reproducibility of the process is important, together with the results obtained in the LSPR sensing. The several points were cared to obtain better reproducibility of this methodology. The careful points for the preparation of LbL film are summarized in Figure S1.

**(i) Preparation of LbL films of AuNP and the gold raspberry.**

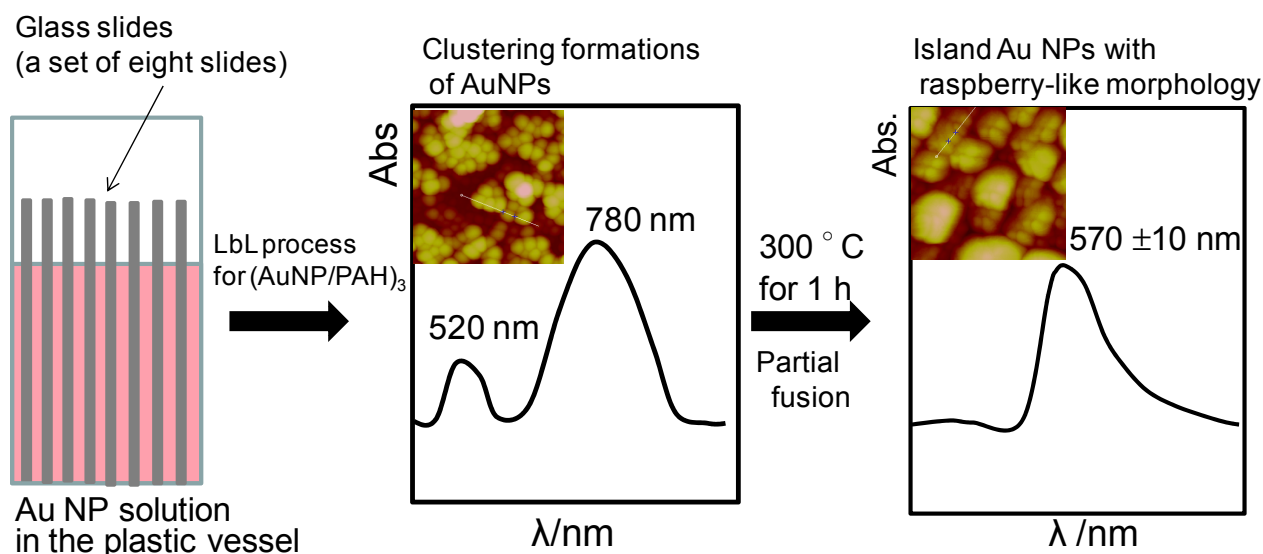
Firstly, it was very important that the glass slides are vertically-installed in the Au NP solution of the plastic vessel in the LbL preparation, as shown in Figure S2(a). When the glass slide was transversely-installed in the Au NP solution, the LbL films of AuNP were obtained with poor reproducibility. To avoid the adsorption of Au NPs into the vessel wall, we used the plastic vessel, instead of glass vessel.

Secondly, it was important to confirm the UV-vis spectra of the immobilized Au NPs on the substrate in each preparation step of (AuNP/PAH)<sub>3</sub> films. Because the partial aggregated AuNPs in the LbL film act as a template for the temperature-induced self-assembly of AuNPs that produces a film with raspberry-like morphology. In the (AuNP/PAH)<sub>3</sub> films before the thermal annealing, we confirmed an intense band around 780 nm for the (AuNP/PAH)<sub>3</sub> films besides the peak around 520 nm in the spectrum (as shown in Figure 2b(i)), which are characteristic for the partially aggregated AuNPs on the substrate. If we could not observe the intense band at 780 nm within  $\pm 10$  nm (i.e. different peak maxima wavelength) in the LbL film in water, we did not proceed to conduct the thermal annealing for the substrate. After the thermal annealing of (AuNP/PAH)<sub>3</sub> film for 24 hours, we checked a relatively sharp LSPR absorption band around 570 nm within  $\pm 10$  nm in water, which are originated from the island Au NPs with raspberry-like morphology. It was also confirmed that the intense band around 780 nm almost disappeared in the spectrum (as shown in Figure 2b(ii)). The time for thermal annealing (i.e. 24 hours) varied somewhat between samples.

**(ii) Measurement points in the substrate.**

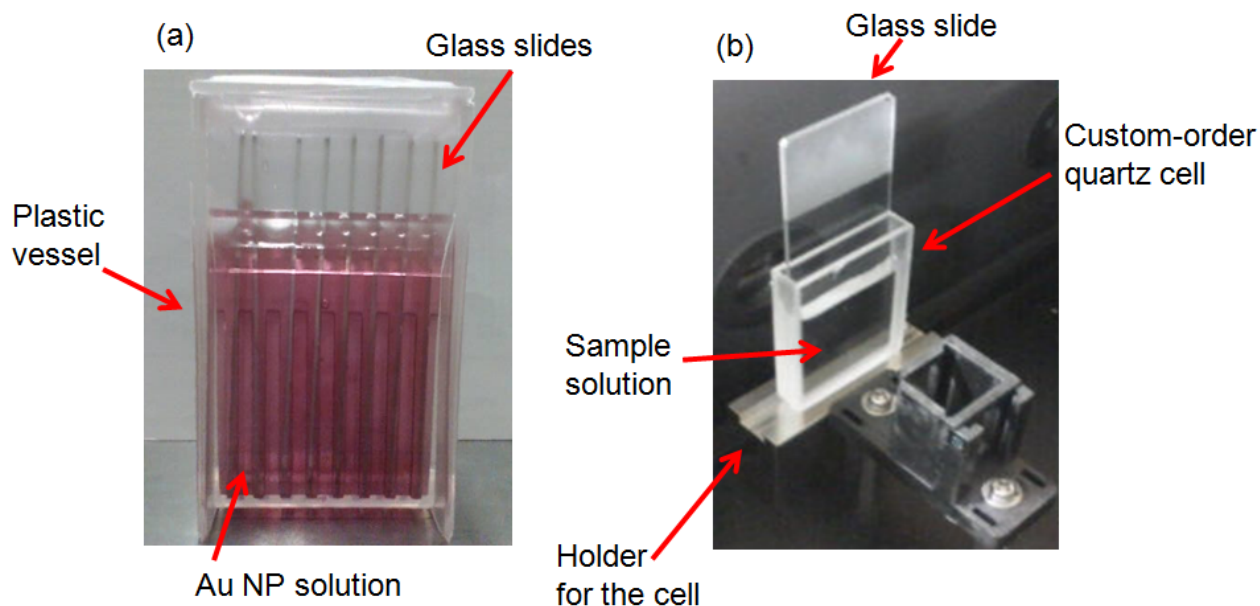
To perform that the measurements have been done in the same substrate position, we prepared a custom-order quartz cell with close-fitting size for the glass slide and the cell holder to fix the quartz cell to the same position in the UV-vis spectrometer, as shown in Figure S2(b). In this system, the glass slide is fixed at a certain position by the use of the holder, and thus measurements at different points on the substrate are difficult.

To satisfy a certain preparation conditions for the LbL films of AuNP, we prepared eight LbL films at the same time, as shown in Figure S2(a). The thermal annealing process for the Au NPs is also performed for the eight glass slides at a time. Among these eight glasses slides prepared thus, there is a small variability from substrate to substrate because of same preparation conditions. The UV-vis spectrum was usually recorded after 10 minutes in immersing the substrate in solution.

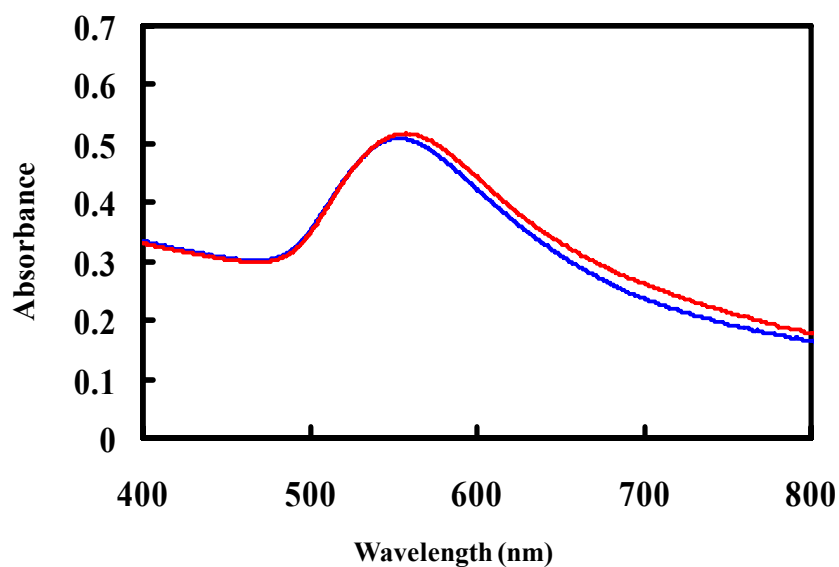


1. Glass slides were vertically-installed in the Au NP solution of the plastic vessel for around 24 h.
2. The spectra show an intense peak at around 780 nm and a weak peak around 520 nm for the (AuNP/PAH)<sub>3</sub> films. Subsequently, the thermal annealing at 300 °C for 1h was conducted.
3. LSPR absorption band was observed around 570 nm within  $\pm 10$ nm, and the intense band around 780 nm almost disappeared in the spectrum. These were characteristic for the island Au NPs with raspberry-like morphology.

**Figure S1.** The procedure for island Au NPs with raspberry-like morphology on glass slide is schematically shown.



**Figure S2.** (a) eight glass slides are vertically-installed in the Au NP solution of the plastic vessel. (b) To perform that the measurements have been done in the same substrate position, we prepared a custom-order quartz cell with the close-fitting size for glass slide and the cell holder to fix the cell with the same position in the UV-vis spectrometer.



**Figure S3.** UV-vis spectra of a raspberry-like assembly of AuNP films in the absence (blue line) and the presence (red line) of MUA layer.