

Supporting Information

In situ SERS Characterization of Emulsifiers at Lipid Interfaces using Label-free Amphiphilic Gold Nanoparticles

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Particle size distributions of gold nanoparticles (GNPs) made from sodium citrate and H₂AuCl₄ were carried out using a dynamic light scattering device (Nano-ZS, Malvern Instruments, Worcestershire, UK) (**Figure S1**). The mean particle diameter (Z-average) calculated from the particle size distribution was 24 nm.

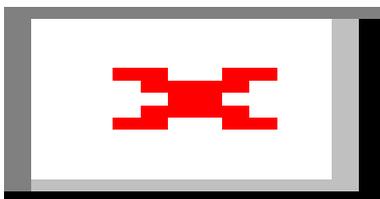
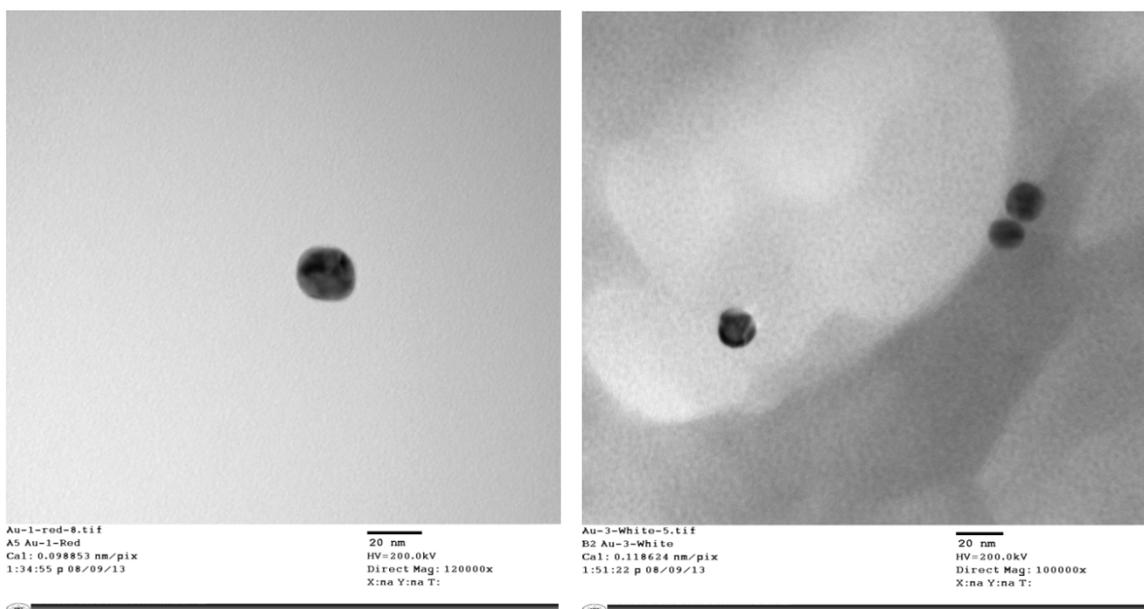


Figure S1. Particle size distributions of GNPs made from sodium citrate and H₂AuCl₄.

Visual observations by transmission electron microscope (TEM) of the modified amphiphilic GNPs showed no obvious differences to those of unmodified hydrophilic GNPs (**Figure S2**).

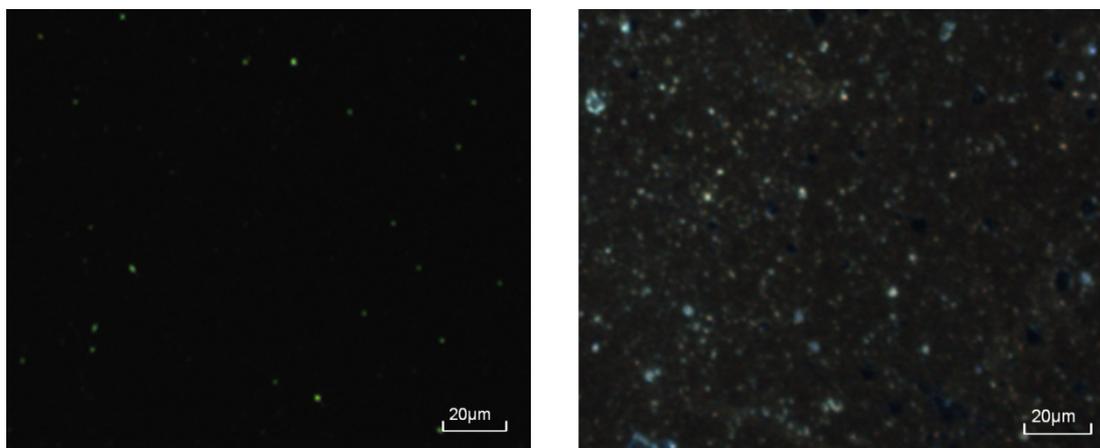


(a)

(b)

Figure S2. TEM of (a) modified and (b) unmodified GNPs.

Under dark-field microscope, the unmodified GNPs in aqueous phase reflected green light, due to the surface plasmon resonance (SPR) peak at around 550 nm (green) (**Figure S3a**). After 12 hrs incubation with octanethiol, a significant increase in the amount of GNPs was observed in the interfacial layer, and the color shifted to blue, indicating conjugation with ligand molecules (**Figure S3b**).



(a)

(b)

Figure S3. Dark-field light-scattering images of modified and unmodified GNPs. (a) Unmodified

GNPs in aqueous phase. (b) Modified GNPs at Hexane/Aqueous Interfacial layer.

The spectra of the GNPs before and after modification were the average of 10 spectra collected. The statistical analysis (principal component analysis) was plotted in the **figure S4**. In the PCA plot, we can clearly see these two sample data points were distinctly separated, indicating their SERS patterns were statistically different.

Figure S4. A PCA plot of the SERS spectra of GNPs before (+) and after (o) modification.

The water-in-oil emulsions containing amphiphilic or hydrophilic GNPs had different optical properties when observed by dark field light scattering microscopy (**Figure S5**). Few bright circles were observed around the water droplets in the emulsion made with amphiphilic GNPs (**Figure S5a**). On the other hand, bright circles were observed at the edge of the water droplets in the samples containing hydrophilic GNPs (**Figure S5b**) or no GNPs (**Figure S5c**). The fact that light scattering from the water droplets was only altered in the presence of amphiphilic GNPs, suggests that they were adsorbed to the droplet surfaces.

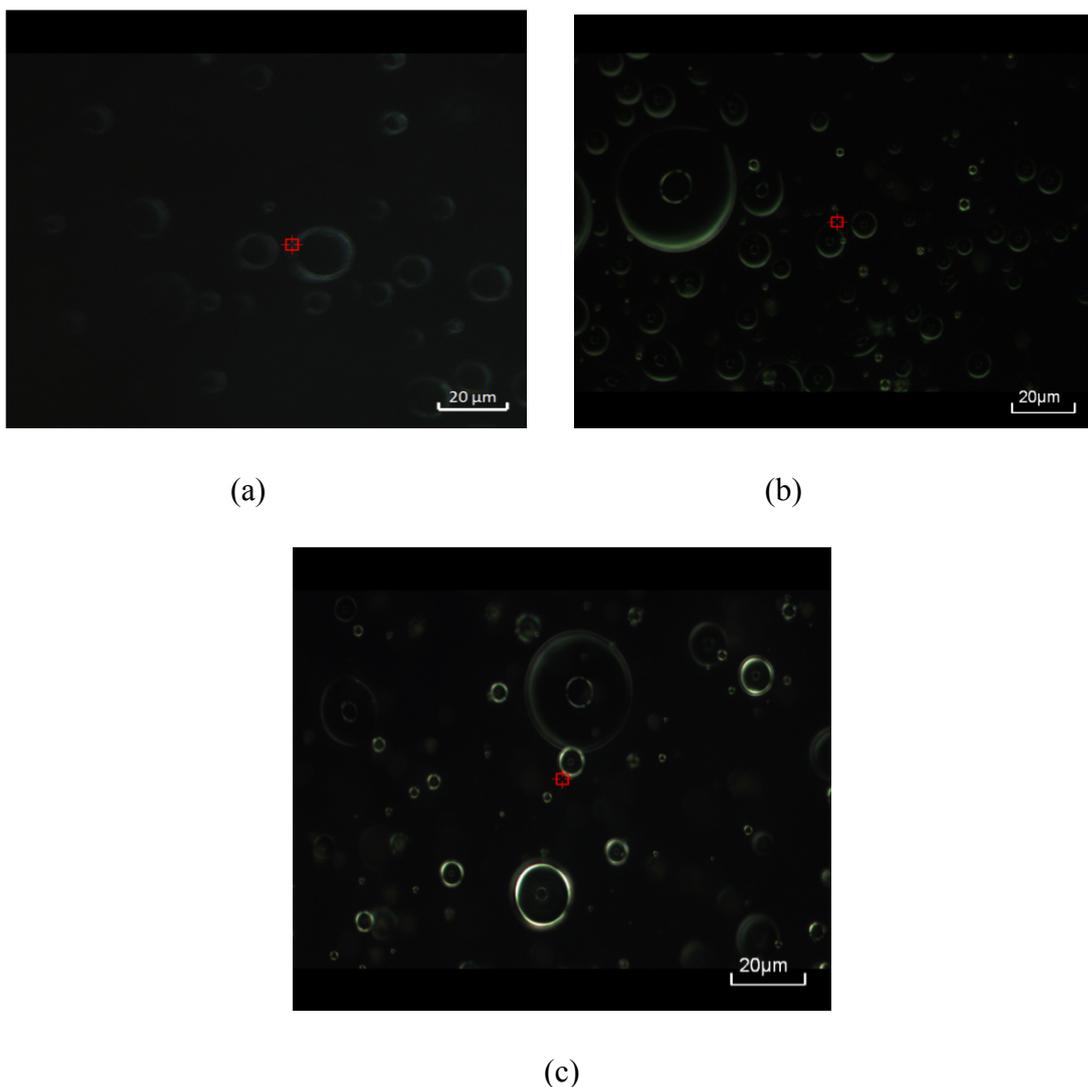
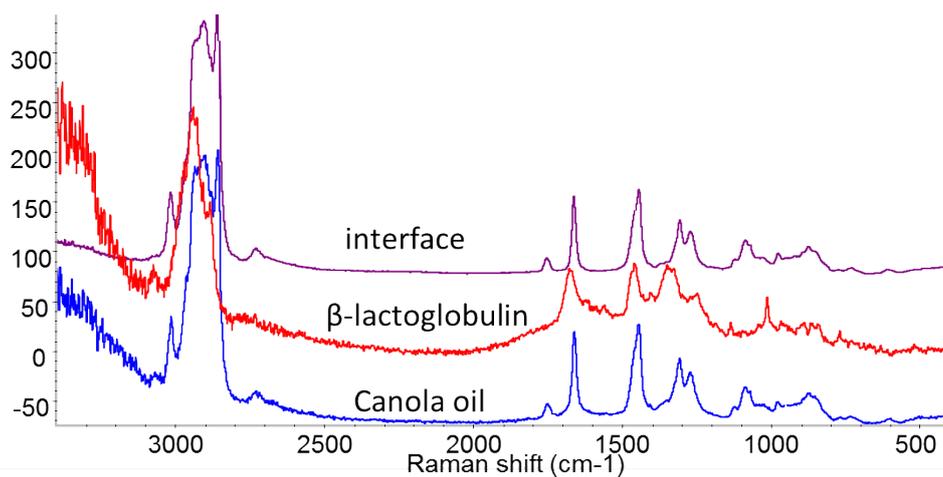
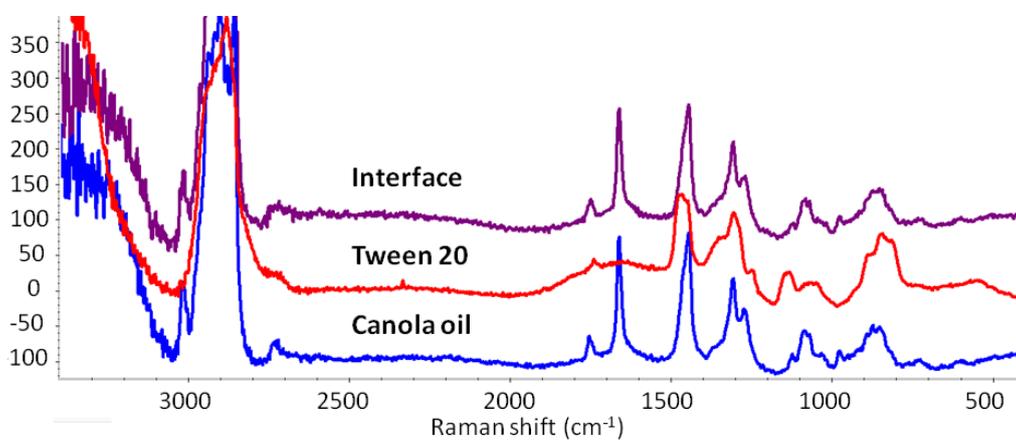


Figure S5. Dark field image of (a) W/O emulsion with modified GNPs, (b) W/O emulsion with unmodified GNPs, and (c) W/O emulsion without GNPs.

No emulsifier signal (neither Tween 20 nor β -lactoglobulin) was observed at the interfacial layer for emulsions without modified GNPs (**Figures S6a and S6b**). Instead, only oil signals were detected. The weak signal from the emulsifier at the interface was obscured by the strong signal from the canola oil because the thin interfacial layer (< 10 nm) only makes up a very small part of the laser detection area (3000 nm).



(a)



(b)

Figure S6. (a) Raman spectra of Tween 20, Canola oil and the interface of the emulsion (without modified GNPs) made from Tween 20. (b) Raman spectra of β -lactoglobulin, Canola oil, and the interface of the emulsion (without modified GNPs) made from β -lactoglobulin.