Electronic Supplementary Information (ESI):

Ionic surfactant-mediated Langmuir-Blodgett method to construct gold nanoparticle films for surface-enhanced Raman scattering

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Fig. S1 (a) Plasmon extinction spectra of 80-nm gold nanoparticle colloid (black line) and 80-nm gold nanoparticle film (red line). The dotted blue line represents a wavelength of excitation laser at 785 nm. (b) TEM and (c) SEM images of 80-nm AuNPs.
Fig. S1 shows (a) plasmon extinction spectra, (b) TEM, and (c) SEM images of 80-nm gold nanoparticles used to fabricate a gold nanoparticle film. The plasmon extinction spectrum from gold nanoparticle film was measured by an inverted microscope (IX70, Olympus, Japan) coupled with a polychromator (Pro-275, Acton) with a thermoelectric cooling charge-coupled device (DV434-FI, Andor), which was the same machine presented in Ref 1. A white light from a 50 W halogen lamp was illuminated through a dark-field and bright-field condenser to the surface of a glass slide on which Au film was deposited. The light from a sample was collected with a 10X objective lens and led to a detector. For gold colloid, plasmon extinction spectrum was measured by a conventional spectrophotometer (Shimadzu UV-3101PC). Due to a few layers of gold nanoparticle film, the extinction signal was not strong as that from gold colloid, and finally plasmon extinction spectrum shows a lot of noise. When the gold nanoparticle film was formed, there was a new plasmon extinction maximum around 800 nm–which is close to the excitation wavelength of 785 nm (See Fig. S1a). It is because the connection of gold nanoparticles decreases the restoring force of plasmonic oscillation on the metal surface, which causes the plasmon oscillation of lower frequency or longer wavelength.

Reference

Fig. S2 (a) Collapsed gold nanoparticle film due to excessive added ethanol. (b) Gold nanoparticle film formed by fast addition of ethanol and (c) its AFM image.
Fig. S3 (a) AFM image, (b) optical image, and (c) SERS spectrum of drop-casted gold nanoparticle film.
Fig. S4  Raman and SERS spectra of a gold film and related chemicals in the film fabrication.
Fig. S5 Infrared spectra of gold nanoparticle films fabricated by octanethiol- and DTAB-mediated techniques before and after dipping in $10^{-6}$ M CV for 1 hr.

The infrared spectra of gold nanoparticle films in Fig. S5 were monitored via an infrared microscope (Contnium infrared microscope equipped with a MCT detector). The microscope was connected to an infrared spectrometer (Nicolet 6700, Nicolet Corporation). Attenuated total reflection Fourier transform infrared (ATR FT-IR) spectrum of gold films were collected by a homemade Ge µIRE attached on a 15X Cassegrain objective. Before treated with $10^{-6}$ M CV, both octanethiol- and DTAB-mediated films show C–H stretching vibrations of long-chain hydrocarbon in the region of 3,000 – 2,800 cm$^{-1}$. After CV deposition, octanethiol-mediated film show a new peak of ring C–C stretching from CV at 1,580 cm$^{-1}$ while DTAB-mediated film show this peak with the vanishing of C–H stretching vibrations of long-chain hydrocarbon. It indicates that DATB molecules were replaced by CV molecules. Moreover, it suggests that octanethiol is still on the gold surface when CV molecules are deposited.

Reference
Fig. S6  SERS spectra collected from (a) octanethiol-mediated and (b) DTAB-mediated gold films after dipping in $10^{-6}$ M CV. Fresh films and 1-week-stored films were used for comparing the film stability. (c) SERS spectra from DTAB-mediated gold films after dipping in $10^{-6}$ M CV measured from various samples for investigating the reproducibility of SERS measurement.
Fig. S7 SERS spectra of DTAB-mediated silver films with (red) and without CV (black). The inset is an image of silver nanoparticle film constructed by this technique. The enhancement factor of this silver film is \( \sim 1.6 \times 10^6 \).