Electronic Supplementary Information (ESI) for:

Large-scale Gold Nanoparticle Superlattice and its SERS Properties for the Quantitative Detection of Toxic Carbaryl

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1. Experimental Section

Chemical:

3-mercaptopropionic acid (MPA, ≥99%), sodium borohydride ($NaBH_4$, 99%) and carbaryl were purchased from Aldrich. Hydrogen tetrachloroaurate trihydrate ($HAuCl_4$•$3H_2O$, 99.99%, ACS reagent grade) were purchased from Alfa. All of the chemicals were used without further purification. HPLC-grade methanol and ethanol was used as received. Deionized water with high resistivity (18.2 MΩ•cm) was obtained via a TKA GenPure ultrapure water system. All the glassware was thoroughly cleaned with aqua regia ($HCl:HNO_3$ =3:1 vol%), rinsed with ultrapure water, and then dried in an oven prior to use.

Methods:

(1) Synthesis of gold nanoparticles

The gold nanoparticles are synthesized via a modified Brust single-phase method[1, 2]. In brief, 0.25 mmol gold salt ($HAuCl_4 \cdot 3H_2O$) dissolved in methanol (10 mL) was introduced into a three-neck flask and cooled down to a temperature of 0 ºC. Then, 3-mercaptopropionic acid (MPA, 0.2 mL) dissolved in deoxygenated water (10 mL) was added into the flask. Under a high stirring speed, the $NaBH_4$ aqueous solution

(2.5 mmol, freshly prepared in 4 mL ice-cold deoxygenated water) was added into above solution with a rate of 0.08 mL/s. The reaction was proceeded for 1 hour. The crude products were precipitated with methanol and washed via an ultrasonic redispersion-centrifugation process to remove the inorganic (Na, Cl, B), unbound MPA and organic impurities. Finally the products were dried in a vacuum oven (less than 5×10^{-3} Torr) without exceeding 25 ºC.

(2) Fabrication of gold substrate superlattice

In a typical process, the hydroxylated silicon wafer surface was prepared by treating them with 1:3 (v/v) mixtures of 30% hydrogen peroxide and 98% sulfuric acid at 80 °C for 20 min. Then, mercaptopropionic acid (MPA) coated gold nanoparticles (the synthesis process was disclosed in experimental section) were dispersed in a 4:5 (v/v) water/methanol solution with a mass concentration of 2 mg/mL and transferred to a glass beaker with a hydroxylated silicon wafer placed at the bottom. The solution was kept from shaking and direct irradiation of light at a temperature of 25 °C. After twelve days, the gold nanoparticle superlattices with mirror-like appearance were obtained.

Characterization:

The samples on Si wafer were imaged using a FEI Quanta 200F in high vacuum mode at 10 keV and at a working distance of 10 mm. An energy-dispersive X-ray spectrometer attached to the FEI Quanta 200F provided in situ determinations of the composition of the as-synthesized superlattices. TEM images and selected area electron diffraction patterns were obtained on a Philips CM20 electron microscope operated at 200 keV. Samples for the TEM analysis were prepared by spreading a drop of as-prepared gold nanoparticles dilute suspension on amorphous carbon-coated copper grids and then dried in air. X-ray diffraction experiment was carried out on a Rigaku D/MAX-2200 diffractometer equipped with a Cu Kα source (λ=0.154056 nm) operated at 40 kV and 40 mA. The samples for SERS measurements were prepared by evaporating 5 μL of ethanolic solution of the carbaryl on the surface of the gold nanoparticle superlattices. Raman spectra were obtained on a Jobin Yvon (Laboratory RAM HR800) spectrometer employing a 632.8 nm laser beam as the excitation source. The Raman band of a silicon wafer locating at 520 cm^{-1} was used to calibrate the spectrometer. All of the spectra were obtained utilizing a 50× objective lens to focus the laser beam onto a spot with a diameter of 1 μm and ~20 mW laser power. The spectra reported were the result of a single 50 s accumulation.

2. Enhancement Factor (EF) Calculation.

The Raman EF was estimated from the standard equation[3]:

$EF=I_{surf}N_{bulk}/I_{bulk}N_{surf}$ (1)

where, I_{surf} and I_{bulk} are the measured SERS intensities for the probe molecules (carbaryl) adsorbed on the SERS active substrate and measured intensity of normal Raman scattering from a bulk sample, respectively. N_{bulk} and N_{surf} are, respectively, the number of molecules on the SERS substrate and that in the bulk illuminated by the light. The Raman band at 1380 cm^{-1} is chosen, and the average peak intensity from five samples was utilized to calculate the EF of the fabricated SERS substrate.

3. Supporting Figures

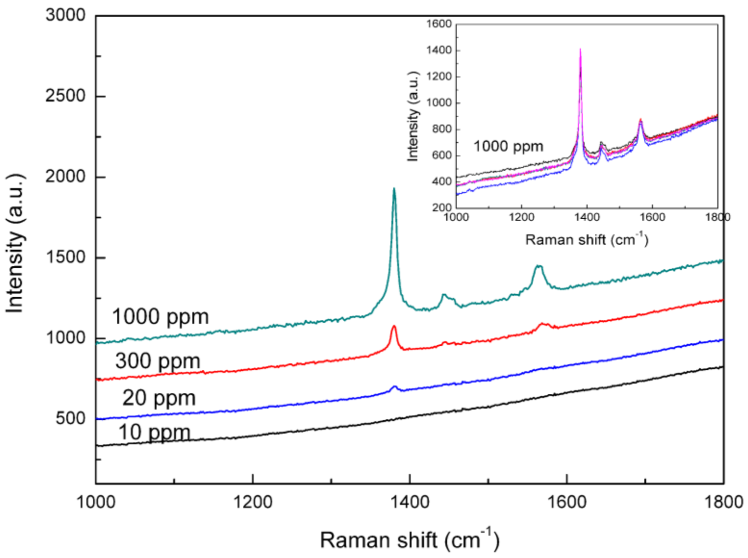

Fig. S1. SERS measurement on the carbaryl with different concentration by using commercially available SERS substrate (Klarite 308, Renishaw). Inset is the reproducible of the substrate measured at concentration of 1000 ppm. It was found that the limit of detection for carbaryl by Klarite 308 is 20 ppm and 20% signal deviation in peak intensities.

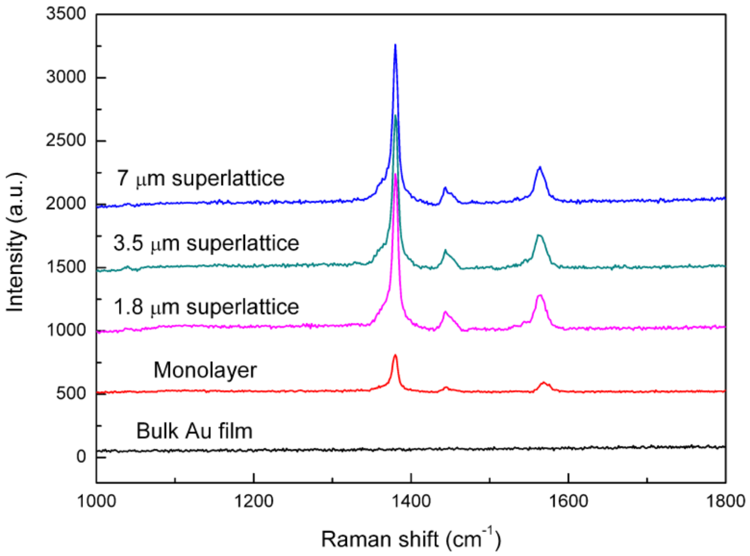

Fig. S2. SERS spectra recorded on the substrates of bulk Au film, monolayer of gold nanoparticles, superlattices with a thickness of 1.8 μm, 3.5 μm and 7 μm. The concentration of carbaryl used is 100 ppm.

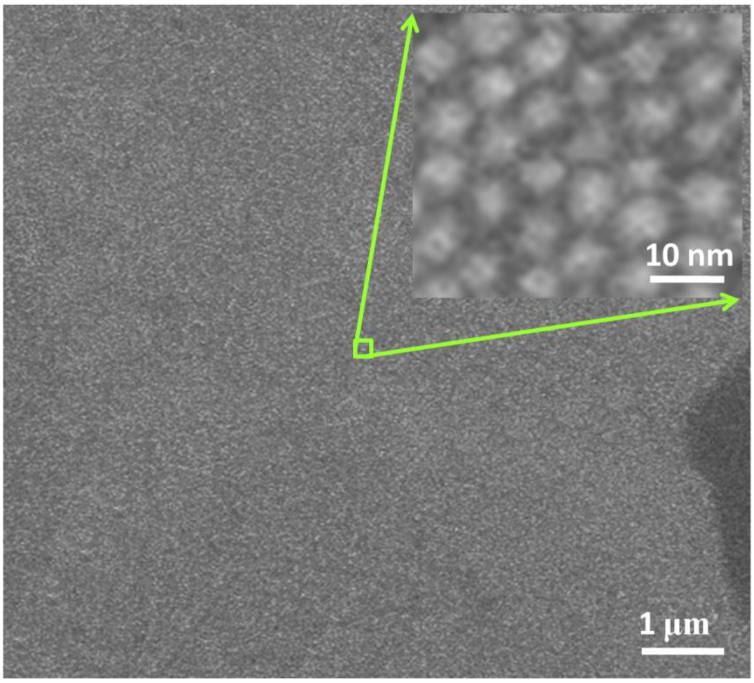

Fig. S3. SEM images of the monolayer of Au nanoparticles, inset being the magnified image.

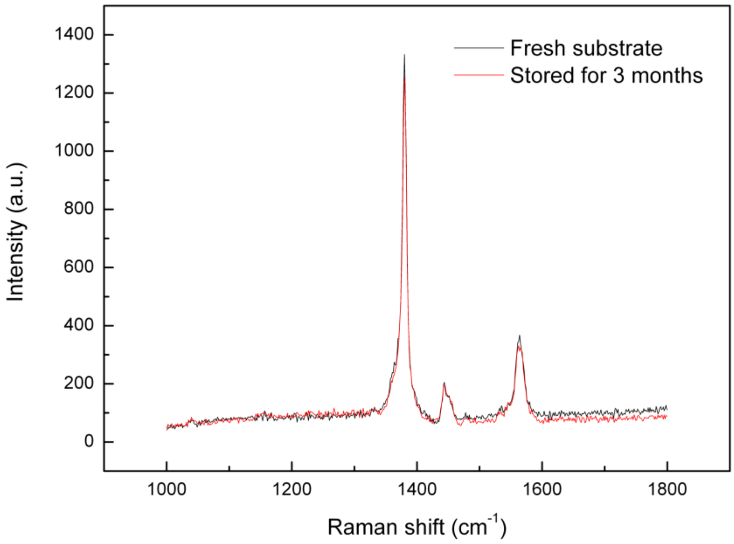

Fig. S4. SERS spectra of carbaryl with a concentration of 100 ppm on freshly fabricated substrate and stored for 3 months.

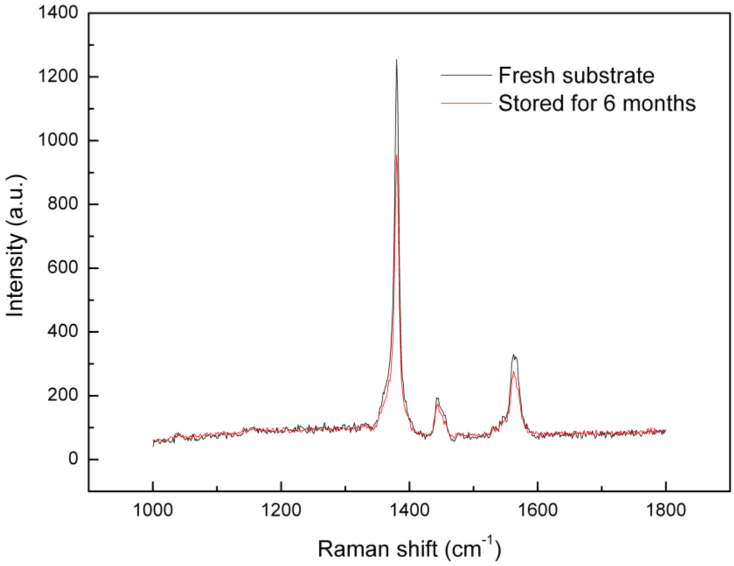

Fig. S5. SERS spectra of carbaryl with a concentration of 100 ppm on freshly fabricated substrate and stored for 6 months.

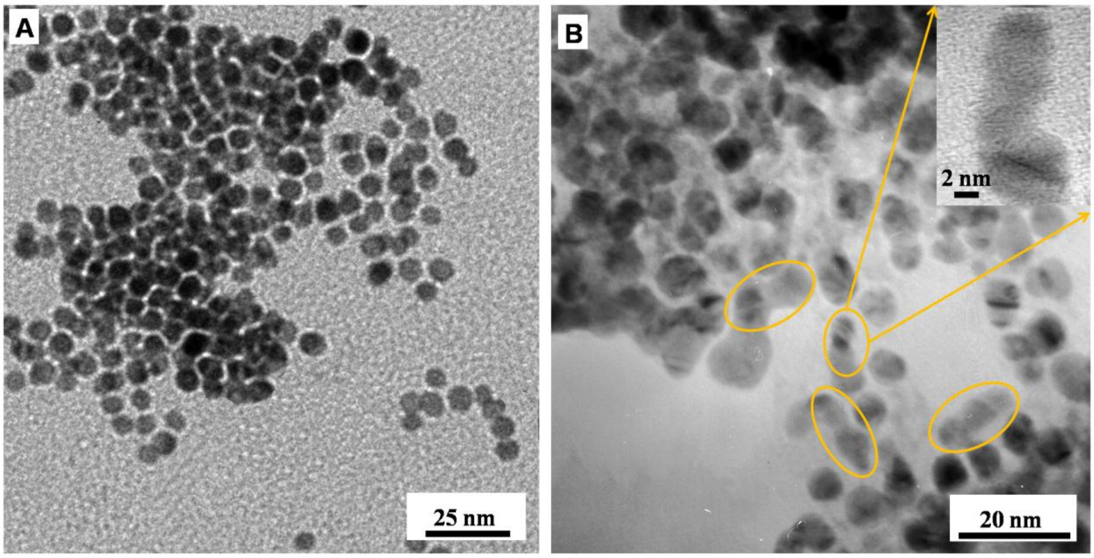

Fig. S6. TEM images of gold nanoparticles samples: (a) prepared by depositing the freshly colloidal solution on the carbon-coated Cu grid; (b) storing the Cu grid deposited with gold nanoparticles for 6 months at ambient atmosphere, inset being the magnified image. The circles show that some nanoparticles have merged into calabash-like nanostructures.

References

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2. Z. J. Wang, L. N. Wu and W. Cai, *Chem-Eur J.*, 2010, **16**, 1459-1463.

3. Z. Q. Tian, J. S. Gao, X. Q. Li, B. Ren, Q. J. Huang, W. B. Cai, F. M. Liu and B. W. Mao, *J. Raman Spectrosc*. 1998, **29**, 703-711.