Electronic Supplementary Material (ESI) for Analyst

Supporting Information

Assembly of polymer-gold nanostructures highly reproducibility into a monolayer film SERS substrate with 5 nm gaps for pesticide trace detection

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S1. SEM of citrate-capped Au NPs and CTAB-capped Au NRs, the close-packed film was not observed.

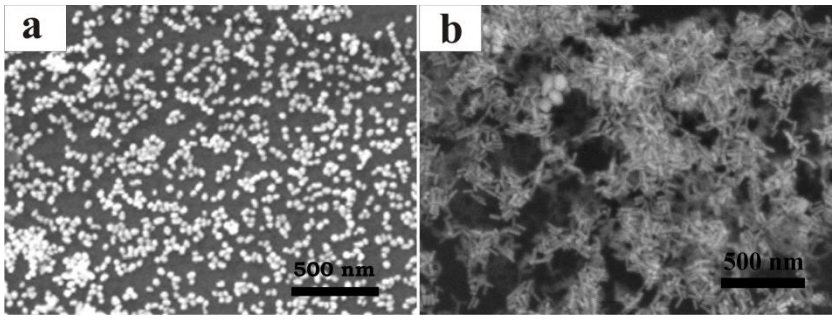

Fig. S1 SEM of (a) citrate-capped Au NPs and (b) CTAB-capped Au NRs, appear random arrangement and the ordering film was not observed.

S2. The amount of mPEG-SH below the critical point, it is not form a high dense degree MLF structure.

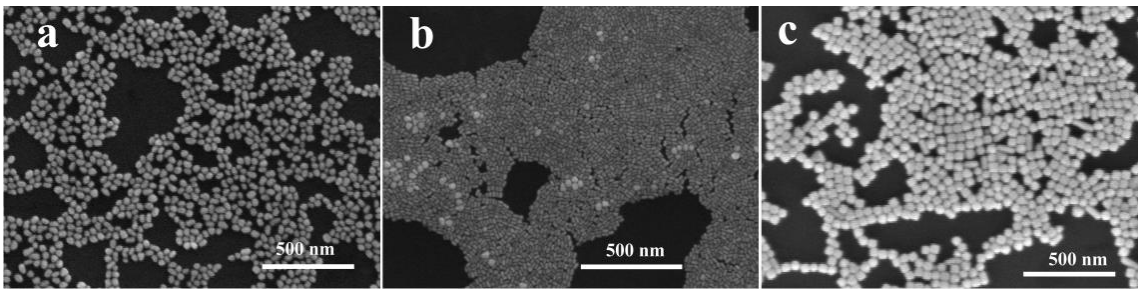

Fig.S2 SEM of (a) Au NPs, CTAB-capped (b)Au NRs and (c) Au NCs after adding amount of mPEG-SH below the critical point, it is not form a high dense degree MLF structure.

S3. The detect limit of the different Au shapes without self-assembly substrates

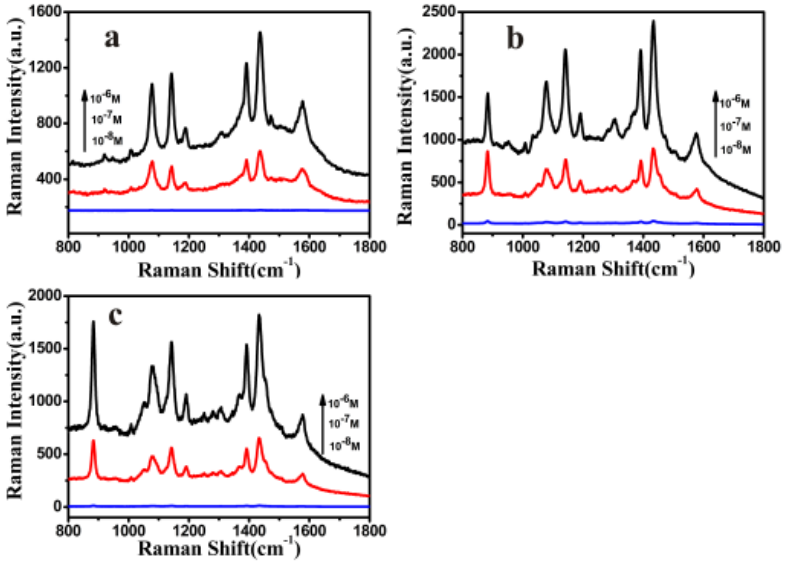

Fig.S3 The SERS spectra of different concentrations of 4-ATP solution collected on the (a) Au NPs, (b) Au NRs, (c) Au NCs MLF substrates without assembly, the detect limit is 10^{-7} M.

S4. The enhancement factor (EF) of different Au shapes with assembly

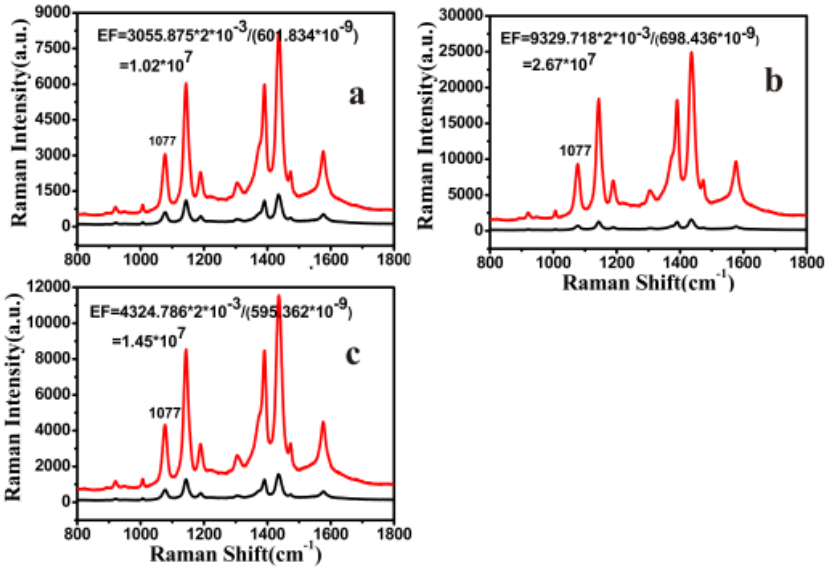

Fig. S4 The enhancement factor (EF) of different samples, (a) Au NPs, (b)Au NRs, (c) Au NCs, the SERS spectra of 10^{-9} M 4-ATP solution (red line) and the normal Raman spectra of 2 mM 4-ATP solution (black line). The EF of different Au nanostructures was calculated to be ~10^7, showing the excellent SERS activity of the substrate.

S5. Discrete dipole approximation (DDA) simulation

The DDA method was used to calculate the near field distributions at the excitation wavelengths of 633 nm. We used an array of closely spaced dipoles to replace a

continuum target with each dipole having a unique polarization under the influence of the electric field of the incident light. Briefly, the incident light is a plane wave along the z-axis, the electric field is polarized along the x-axis. For calculations of two particles, arraying along the x-axis is assumed, so that the longitudinal modes are excited. The electric field pattern crosses over the particle, namely, it yields the field outside and within the particle. Based on the calculation of the ratio of the enhanced field to the incident field, the effect of the field enhancement can then be investigated. Three models have been used in this study, Au nanoparticles (50 nm) dimer, the nanorods dimer with aspect ratios=2, and Au cubes dimer (50 nm), respectively.

Fig. S5a-c show the typical distributions of the electric field strength E calculated in a plane across a vertical axis of these model particles irradiated from above at 633 nm. As one might have anticipated, the most localized and enhanced electric field areas are found in the gap of nanorod by head to head. The maximal enhancement of Au NPs, NCs and NRs is found to be about 13.5, 18.8 and 40.2, respectively. In other words, the nanorod are clearly favored as the one potentially demonstrating the largest SERS enhancement (proportional to $|E|^4$), which is in agreement with the experimental data of sensitivity and enhancement factors of multiple Au shapes monolayer nanoparticles assembly (the table 1 of article).

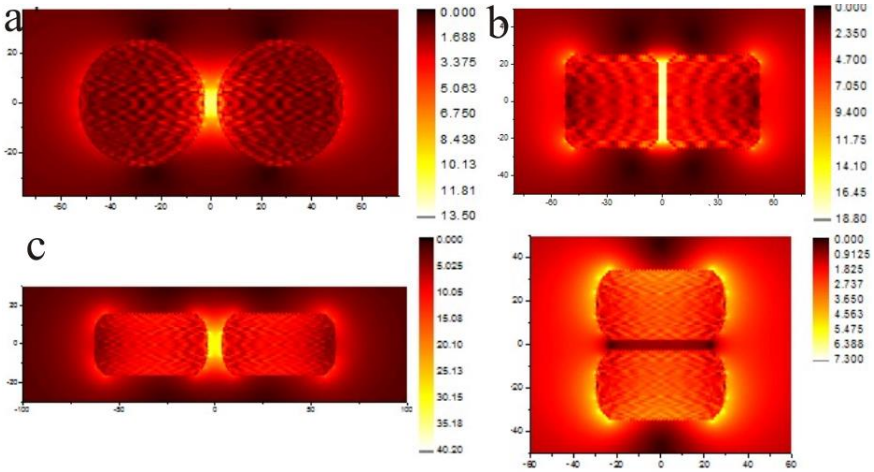

Fig. S5 The local electric field distribution of gold nanoparticles dimer with gaps of 5 nm across air-suspended particles irradiated from top at the wavelengths of 633 nm. a-c corresponding to Au NPs, NCs and NRs. The left of c corresponding to head to head, the right of c corresponding to side by side.

S6: The SERS line-scan spectra and RSD value of Au NP substrate without assembly

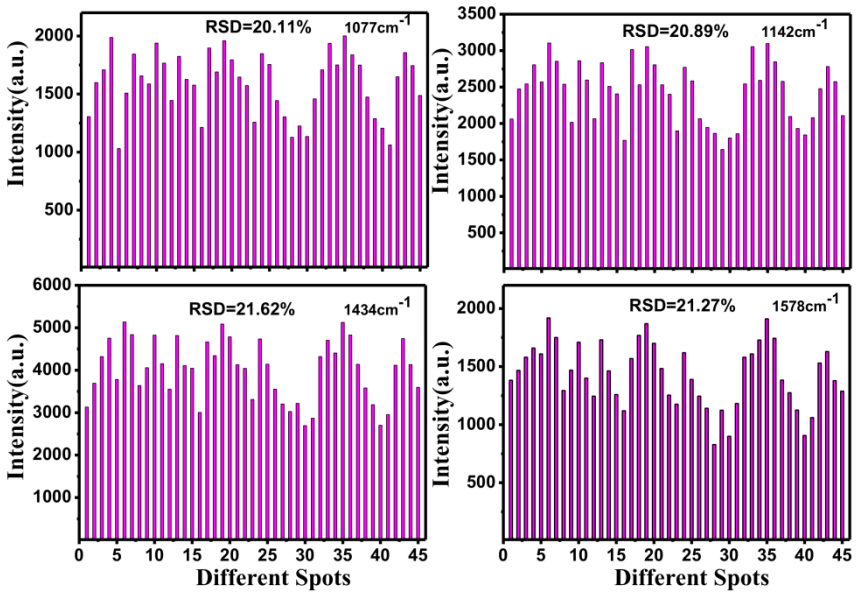

Fig. S6 The intensities of the main Raman vibrations of 4-ATP solution (at 1×10^{-8} M) SERS line-scan spectra in the 45 spots collected on the Au NP not assembly. The RSD value of signal intensities of major SERS peaks is observed to be > 20%, indicating that has a poor reproducibility.

S7: The 3D SERS spectra of paraoxon collected on the assembly and not assembly substrate

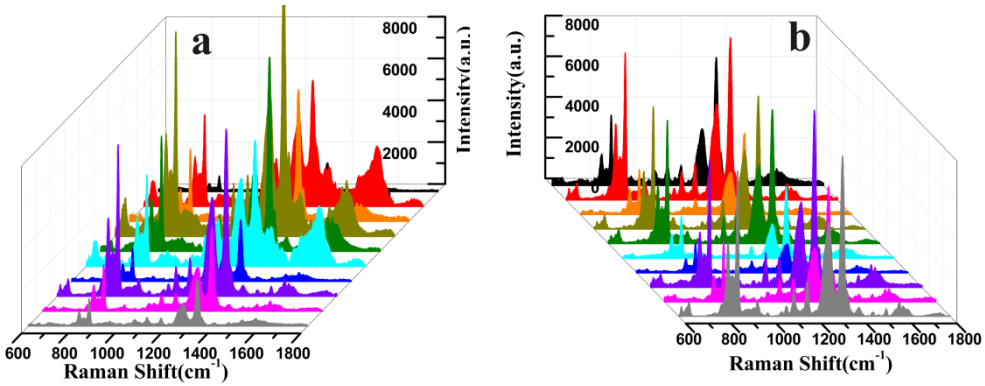

Fig. S7 The 3D SERS spectra of paraoxon solution (at 1×10^{-6} M) in the 10 spots collected on the Au NP (a) not assembly and (b) assembly substrate.