Electronic Supplementary Information

Two-dimension Flower-Shaped Au@Ag Nanoparticle arrays As Reproducible and Highly Sensitive SERS Substrates for Detection of Pesticide Thiram

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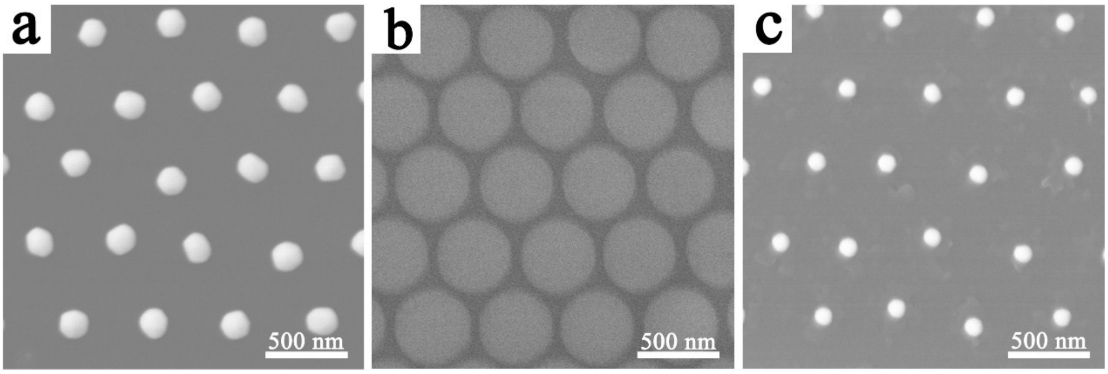

Fig. S1 SEM images of nanoparticle (NP) arrays as the growth template: (a) the hexagonal non-close-packed (*hncp*) Au NP arrays. (b) the *hncp* polystyrene (PS) colloidal microsphere arrays. (c) the *hncp* Cu NP arrays.

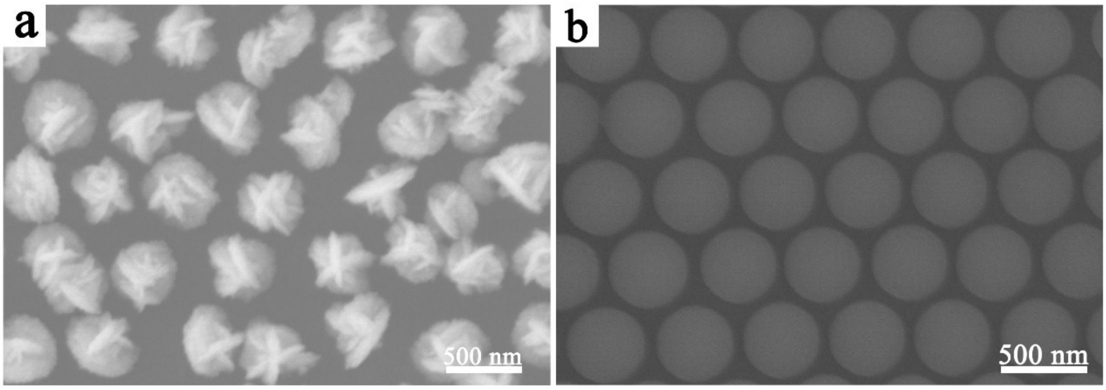

Fig. S2 (a) SEM image of the flower-shaped Cu@Ag NP arrays using *hncp* Cu NP arrays as the growth template. (b) SEM image of the obtained array without Ag nanosheets grown on it using hexagonally patterned PS colloidal microsphere arrays as the growth template.

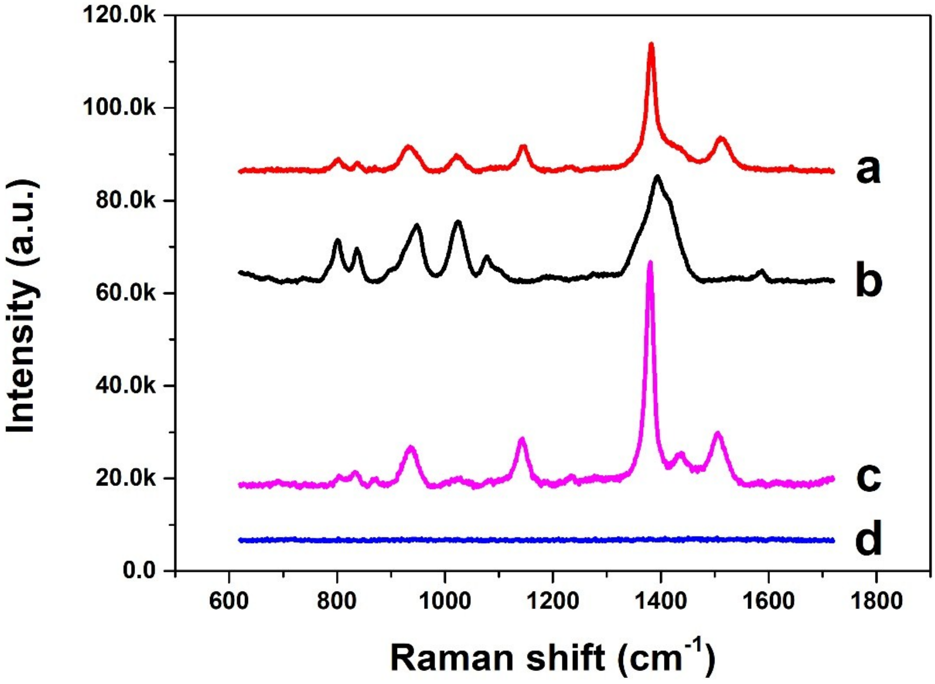

Fig. S3 SERS spectrum of thiram (a) and Raman spectra (b) of the hexagonally patterned flower-shaped Au@Ag NP arrays with citrate surfactant; SERS spectrum of thiram (c) and Raman spectra (d) of the hexagonally patterned flower-shaped Au@Ag NP arrays soaked with potassium iodide.

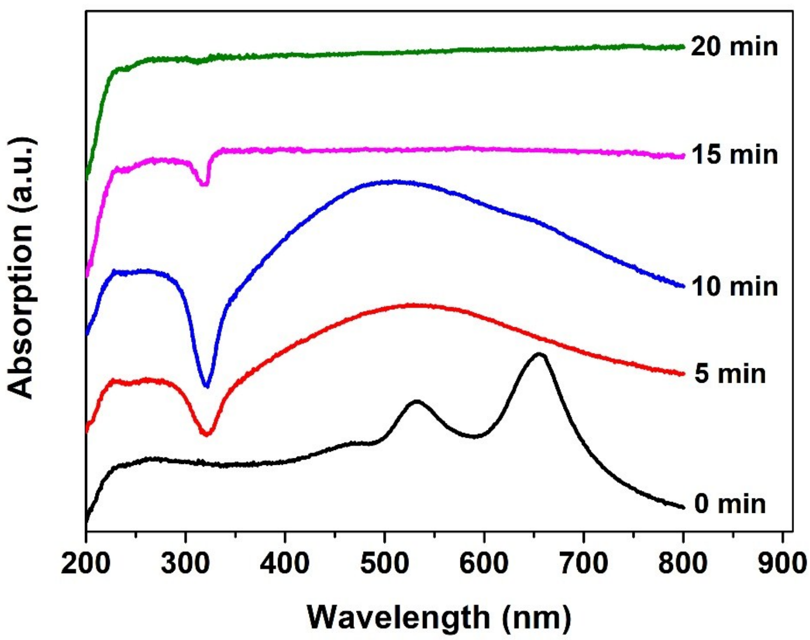

Fig. S4 The extinction spectra of the *hncp* Au NP arrays (0 min) and the hexagonally patterned flower-shaped Au@Ag NP arrays with different growth time (5-20 min).

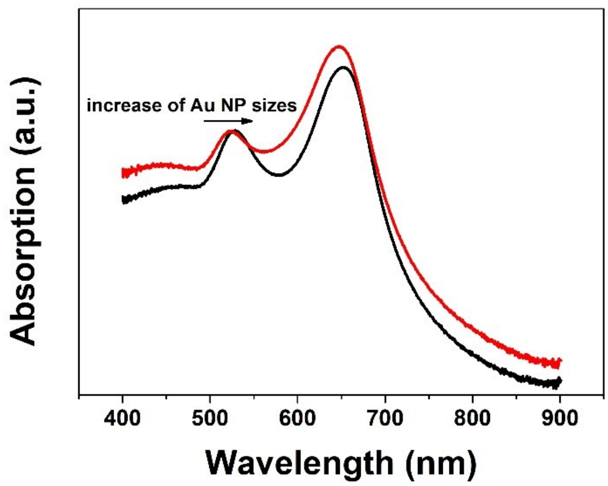

Fig. S5 The extinction spectra of the *hncp* Au NP arrays with different Au NP sizes (red line of 190 nm and black line of 260 nm in diameter of Au nanoparticles).

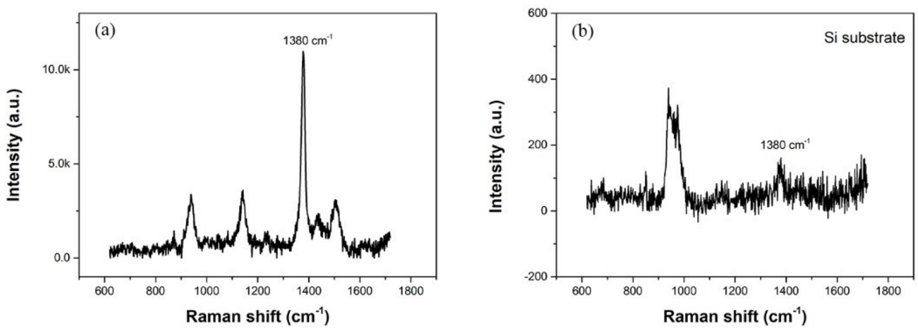

Fig. S6 (a) Raman signal acquired by dropping 5 μl thiram ethanol solution (10^{-7} M) on hexagonally patterned flower-shaped Au@Ag NP arrays (area: 0.5×0.5 cm^2). (b) Normal Raman signal acquired by dropping 5 μl thiram ethanol solution (10^{-2} M) on a silicon substrate (area: 0.5×0.5 cm^2). The SERS detection parameters: integration time: 5 s, power of the excitation laser: 1.25 mW.

The enhancement factor (EF) of hexagonally patterned flower-shaped Au@Ag NP arrays was calculated by the equation:

$$EF = (I_{SERS} / N_{SERS}) / (I_{normal} / N_{normal})$$

Where I_{SERS} and I_{normal} are the intensity of 1380 cm^{-1} peak acquired from thiram (concentration of 10^{-7} M) with hexagonally patterned flower-shaped Au@Ag NP arrays and the normal intensity obtained from thiram (concentration of 10^{-2} M) without the hexagonally patterned flower-shaped Au@Ag NP arrays, respectively. N_{SERS} and N_{normal} are the number of probe thiram molecules being sampled in the SERS and normal Raman detections, respectively. Herein, I_{SERS} (10449.43 counts) and I_{normal} (103.05 counts) could be observed from the spectra directly while N_{SERS} and N_{normal} need to be calculated.

Assume that the laser can completely penetrate the metal nanostructures and the 5 μl drop of thiram molecules dropped onto the substrates were fully adsorbed. Therefore, the number of probe molecules being illuminated by the laser can be calculated as :

$$N_{SERS} = 5\times10^{-6}L\times10^{-7}mol/L\times6.02\times10^{23}mol^{-1}\times\left(\frac{\pi\frac{d^2}{4}}{a^2}\right)=9456$$

$$N_{normal} = 5\times10^{-6}L\times10^{-2}mol/L\times6.02\times10^{23}mol^{-1}\times\left(\frac{\pi\frac{d^2}{4}}{a^2}\right)=9.456\times10^{8}$$

where the diameter of the laser spot (d) is about 1 μm; a is the length of side of substrates, a=5 mm.

Therefore,

$$EF = (I_{SERS} / N_{SERS}) / (I_{normal} / N_{normal}) = 1.01\times10^{7}.$$

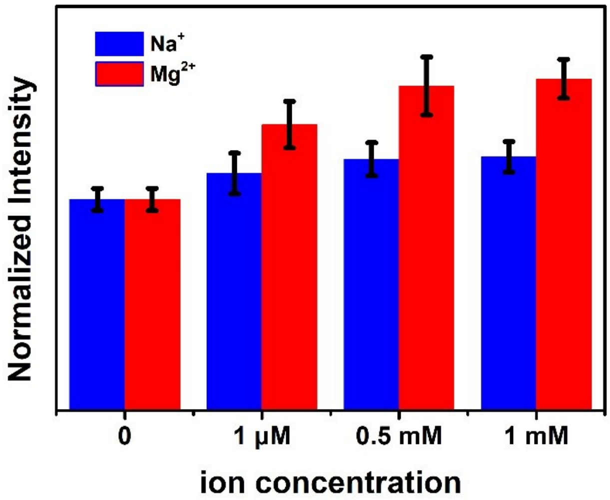

Fig. S7 Effect of inorganic salt ions Na^{+} and Mg^{2+} concentration on the detection of thiram.

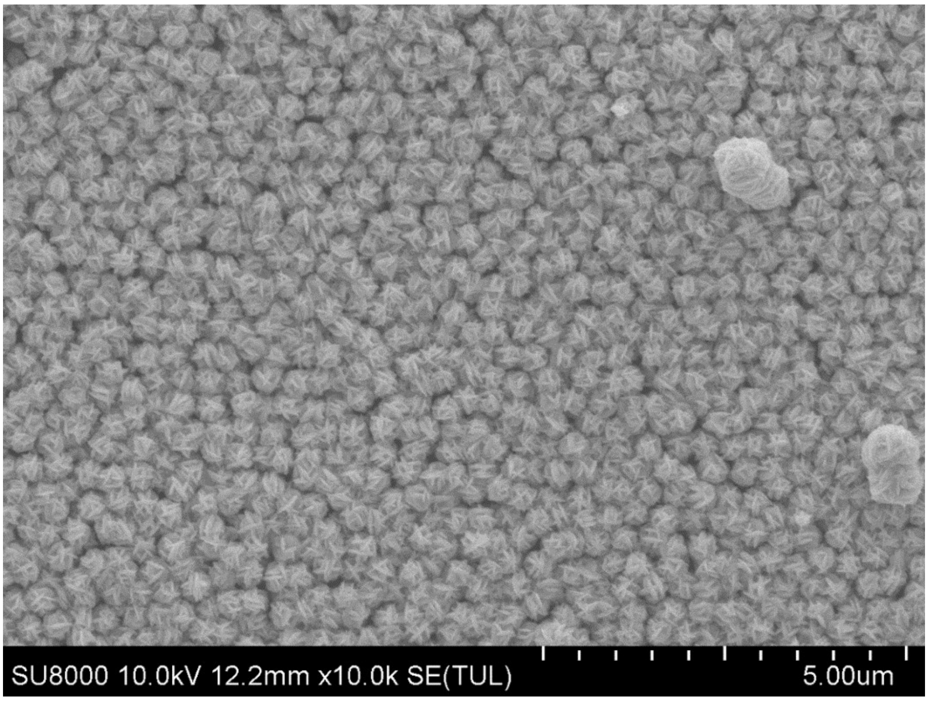

Fig. S8 SEM image of the hexagonally patterned flower-shaped Au@Ag NP arrays with the periodicity of 350 nm.

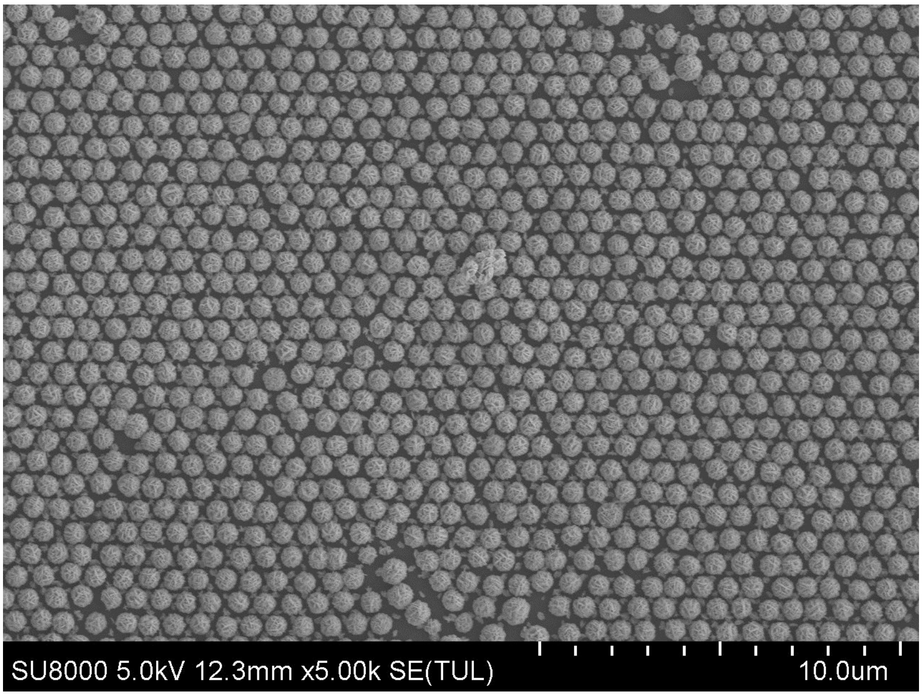

Fig. S9 SEM image of the hexagonally patterned flower-shaped Au@Ag NP arrays with the periodicity of 750 nm.

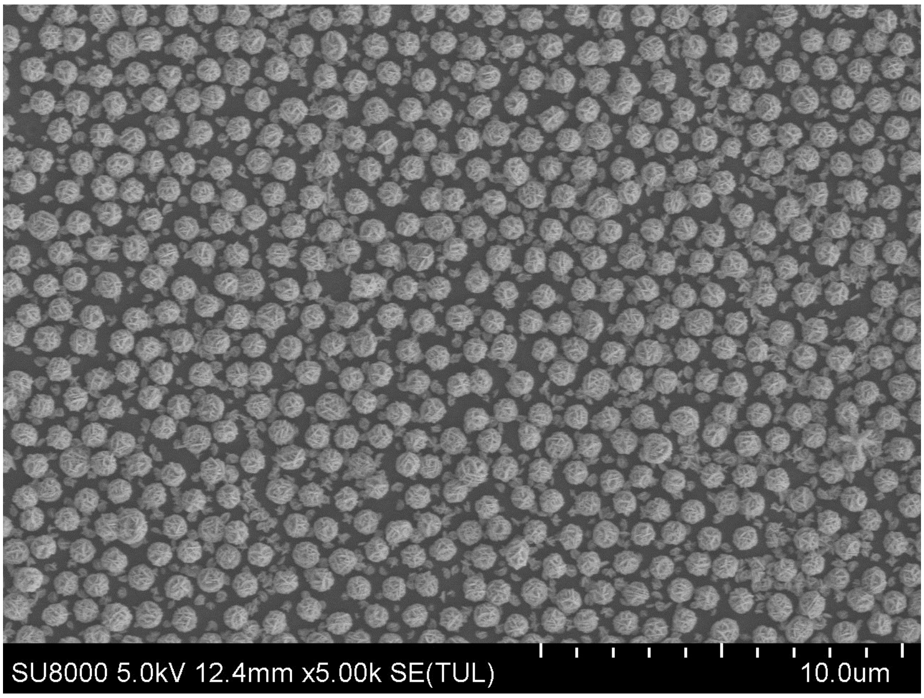

Fig. S10 SEM image of the hexagonally patterned flower-shaped Au@Ag NP arrays with the periodicity of 1000 nm.

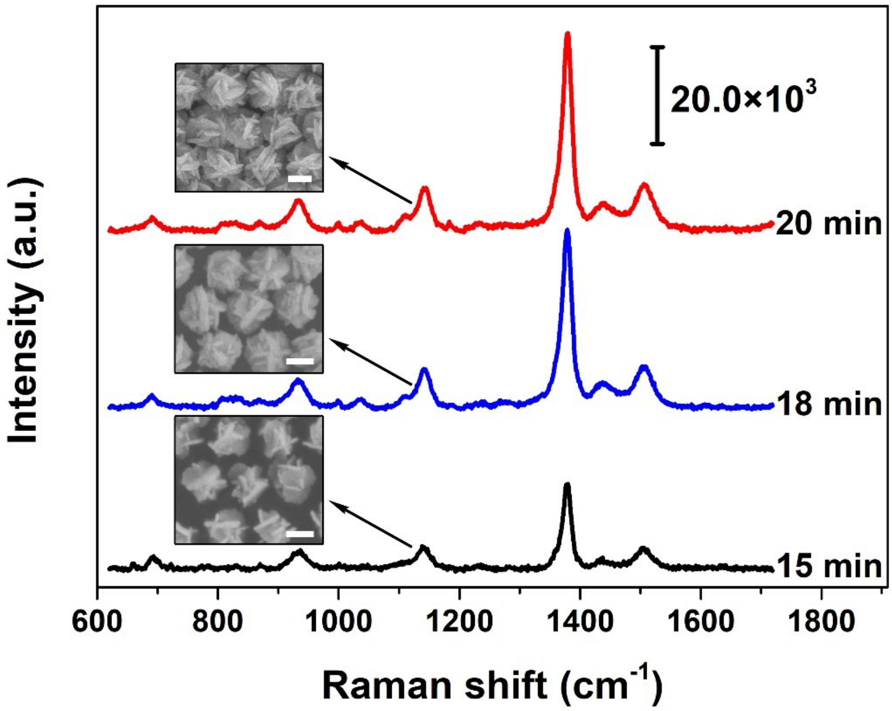

Fig. S11 Raman spectra of 10^{-7} M thiram on the hexagonally patterned flower-shaped Au@Ag NP arrays (350 nm in periodicity) with different growth time (15, 18 and 20 min). Insets: corresponding SEM images. Scale bars in insets: 200 nm.