Electronic Supplementary Material (ESI) for Analyst.
This journal is © The Royal Society of Chemistry 2015

Supporting Information

Experimental Section

Materials and instruments. Silver nitrate ($AgNO_{3)}$ and citric acid were obtained from Shanghai Chemical Reagent Company (Shanghai, China). Rhodamine 6 was obtained from Sigma Company (Shanghai, China). All reagents were of analytical grade and used as received without further purification. Ultrapure water (>18.0 M•cm) was purified using a Millipore Milli-Q (Suzhou, China) gradient system through-out experiment. SERS measurements were carried out with a confocal microprobe Raman system (LabRam HR800) using a laser of 532 nm. The scanning electron microscopy (SEM) images were taken by a field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F, 10 kV).

Treat the quartz glass into hydrophobic surface. Firstly, quartz glass sheets were cleaned by immersion in a boiling solution prepared by mixing 30% H_2O_2 and concentrated H_2SO_4 with a volume ratio of 1:3. After cooling, the substrates were rinsed repeatedly with ultrapure water. Then, immerged into 40 mM triethoxy-1H,1H,2H,2H-tridecafluoro-n-octylsilane solution for 2 hours. Finally, dried with nitrogen atmosphere for 30min at room temperature.

Preparation of silver colloidal suspension. Before the preparation of Ag nanospheres, all glassware was cleaned in a bath of freshly prepared aquaregia (HCl/HNO_3 3 : 1) and then rinsed with deionized water prior to use. The silver nanoparticles were synthesized by the citric acid reduction method. The mole ratio of citric acid to $AgNO_3$ was 1:4. In a typical synthesis, 100 mL $AgNO_3$ (10^{-3}M) was heated until boiling. Then, 4 mL of 1% sodium citrate solution was added into the boiling solution and the boiling maintained for an hour. The synthesized colloidal AgNPs were characterized by scanning electron microscopy (SEM). The AgNPs in the suspension have a diameter of approximately 50 nm.

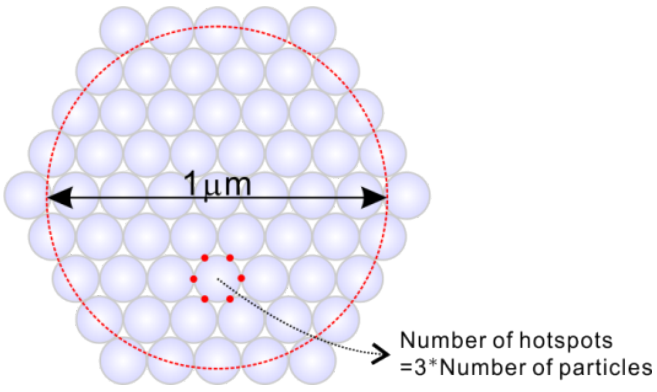

Figure S1. The ideal 2D closely-packed assembly of nanospheres and each particle forms six hotsopts with the surrounding particles.

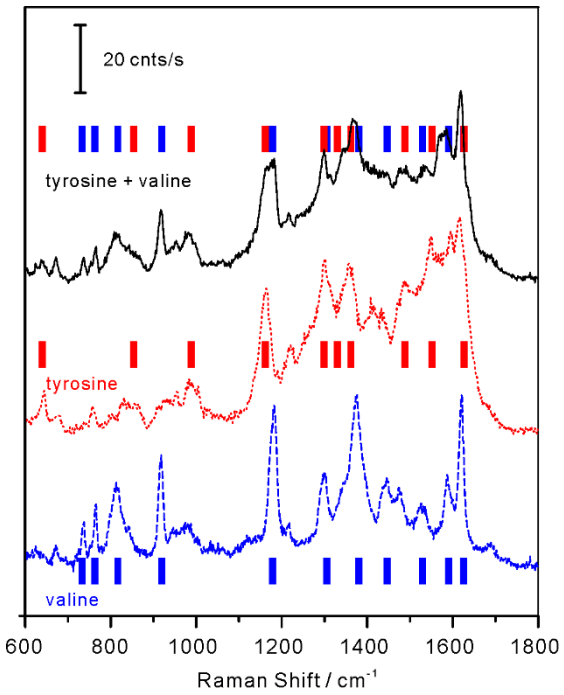

Figure S2. SERS spectrum for the multiplex detection of tyrosine and valine (top). Individual SERS spectra of tyrosine in the aqueous phase (middle) and valine in the aqueous phase (bottom) at the same respective concentrations (0.5 pmol) are included for comparison.

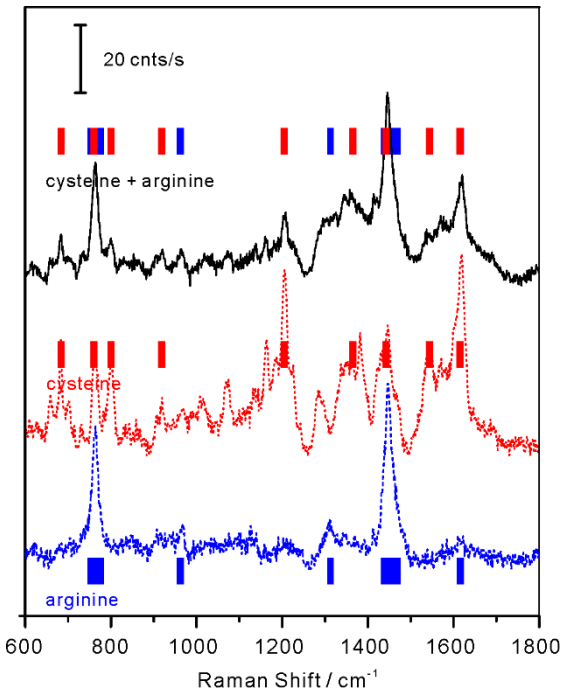

Figure S3. SERS spectrum for the multiplex detection of cysteine and arginine (top). Individual SERS spectra of cysteine in the aqueous phase (middle) and arginine in the aqueous phase (bottom) at the same respective concentrations (5 pmol) are included for comparison.