Electronic Supplementary Information for:

Facile and rapid fabrication of large-scale silver nanoparticles arrays with high SERS performance†

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Experimental details

Figure. S1-9

Experimental Section

Chemicals and reagents

Trisodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$, 99%), Rhodamine 6G(R6G,95%) and ascorbic acid (Vc, ≥99%) were purchased from Aladdin, silver nitrate ($AgNO_3$, ≥99.8%) from Shanghai SSS Reagent Co.,Ltd., hydrogen nitrate (HNO_3,65%-68%), sulfuric acid (H_2SO_4, 95-98%), hydrogen peroxide (H_2O_2, ≥30%) and ethanol (C_2H_6O, ≥99.7%) from ChengDu Kelong Chemical Co.,Ltd., All reagents were used without further purification. Ultrapure water (resistivity >18.0 MΩ cm) was used throughout the experiments.

Sythesis of AgNPs Colloid

Citrate-reduced silver colloid was synthesized according to Lee and Meisel's method.[1] A 90 mg amount of $AgNO_3$ was dissolved in 100 mL of H_2O, and heated to boiling. Then an amount of 2 mL of 38.8 mM sodium citrate was added dropwise with fast stirring. The mixture was allowed to be kept boling for 15 min and was allowed to cool to room temperature under stirring. These silver nanoparticles are well-known to have a mixture of sizes and shapes, including rods, spheres, and prisms.[2]

Self-assembly of large-scale AgNPs arrays on Si/glass substrates

Large-scale AgNPs arrays on silicon/glass wafers were prepared through utilizing Vc as an active reagent to control self-assembly. In a typical process, 0.5 mL of 100 mM Vc was added into 20 mL of silver colloid under stiring. Silicon/glass wafers were cleaned using ultrapure water, ethanol and ultrapure water in sequence and then dried under nitrogen atmosphere. Then, several pieces of these cleaned Si substrates, without any need for further surface modification, were immersed into the Vc-activated silver colloid for approximately 1 hour. Glass substrates were treated with a mixed solution of H_2O_2 (30%) : H_2SO_4 (98%) = 3:7 for 20 min at 120℃, cleaned with ultrapure water, and immersed into the Vc-activated silver colloid for 1 h. Thus, large-scale AgNPs arrays were consciously self-assembled onto the surface of Si/glass substrates. To demonstrate the influence of Vc on the self-assembly behavior of AgNPs, four solution samples were prepared by adding 0.1, 0.3, 0.5 and 1 mL amount of Vc into 20 mL of silver colloid respectively, and the corresponding self-assembly SERS substrates on silicon/glass wafers were denoted as A, B, C and D by depositing 1 h. The main virtue of this self-assembly method is that it can be able to derectly deposit silver nanoparticles on Si substrates without special substrate surface modifications, while in previous work, AgNPs usually assembled onto the surface of substrates functionalized with 1,10-phenanthroline[3] or aminopropyltriethoxy-silane[4]. Morever, another advantage of this method is that the density of AgNPs deposited on silicon wafers could be conveniently tuned by adjusting the amount of Vc.

Measurements

TEM observations were obtained by using a transmission electron microscope (TEM, FEI, F20) with an operating voltage of 200kV. Samples for TEM were prepared by immersing carbon-coated copper grid into diluted AgNPs colloids for several seconds and dried at room temperature. SEM images were gained by using a field-emission SEM (FEI, Sirion200). Absorption spectrum were collected on a UV-vis spectrophotometer(SHIMADZU UV SPECTROPHOTOMETER, UV-1800). The pH of Vc-activated silver colloid was obtained by a pH meter (Shanghai Yueping scientific instrument Co., Ltd., PHS-25).

SERS measurements: A LabRam Xplora confocal Raman Spectrometer (Horiba Jobin Yvon) was used for SERS spectral measurments. Rhodamine 6G (R6G),a strongly fluorescent xanthene derivative that shows a molecular resonance Raman effect when it was excited in visible light region, was used as the probe molecular for SERS analysis. For each sample, we took five different positions of the substrate randomly for Raman measurements, and the SERS intensity was obtained by averaging them. To prepare the substrate for R6G detection, A droplet containing 5 μL amount of R6G water solution was dropped onto the surface of the SERS substrate, then dried in air for 2 min to immobilize the molecules on the substrate surface before SRES measurement. In order to get high spatial resolution, the Raman scattering signal was collected with a high numerical aperture (NA) microscope objective from Olympus (100×, NA=1.40). Two linear-polarized lasers with excitation wavenumber of 532 nm (0.025 mW) and 638 nm (0.24 mW) were used for the excitations. The exposure time of Raman measurement was 5 s for 532 nm laser and 1 s for 638 nm laser. In order to determin the EF of the fabiricated SERS surbstrate, a 5 μL amount of 10^{-3} R6G was placed onto silicon wafer and a 5 μL amount of 10^{-7} R6G was droped onto SERS substrate C.

Demonstration of the role of Vc on the self-assembly behavior in silver colloids. To show the important role of Vc playing in self-assembly, two solution samples having different ingredients were prepared. One contained silver colloid and Vc, another contained only silver colloid. Then, silicon wafers were immersed into the two sample solution for 20 h. Figure. S1 shows the photographs of two silicon wafers. It shows clearly that the surface of Si immersed in the AgNPs containing Vc deposite a uniform Ag film, while there are few Ag depositing on the surface of that immersed in the AgNPs containing no Vc. Therefore, we demonstrate that Vc plays the key role in the preparation of self-assembled AgNPs films in aqueous AgNPs solution.
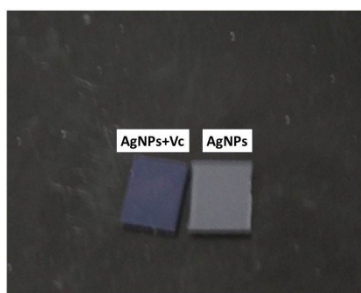
Figure. S1　Photographs of two silicon wafers after 20 h immersion in AgNPs colloid by adding Vc (the left) and no Vc (the right).

The effect of Vc on the state of AgNPs aggregation. To investagate the effect of Vc on the state of AgNPs aggregation, five solution samples were prepared by adding 0.1, 0.3, 0.5, 1.0, 2.0 ml Vc into 20 mL silver colloid, respectively. Figure. S2 shows the photographs of the solution samples. It exhibits clearly that the AgNPs of samples D and E aggregate and precipitate partially because large amount of Vc give rise to the decrease of the pH and cause the instability of silver colloid. That is to say, Vc is a double-edged sword, and the reaction is a competing process between self-assembly of AgNPs and aggregation of AgNPs.
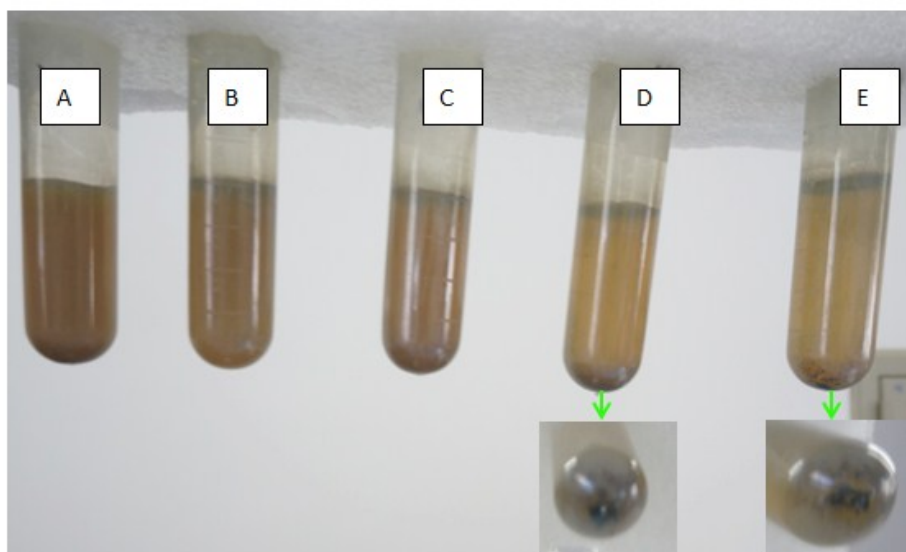
Figure. S2 Photograph comparisons in 20 mL silver colloid after adding different amount of 0.1 M of Vc. A, 0.1 mL. B, 0.3 mL. C, 0.5 mL. D, 1.0 mL. E, 2.0 mL.

The effect of Vc on the self-assembly of AgNPs on silicon wafer in aqueous solution. Four substrates which are denoted as A, B, C, D with different amount of Vc were prepared. Figure. S3 shows the photographs of substrates, we can see that the deposition density of substrates B, C, and D are larger than that of substrate A , conform with the result of SEM images (see Fig.2).
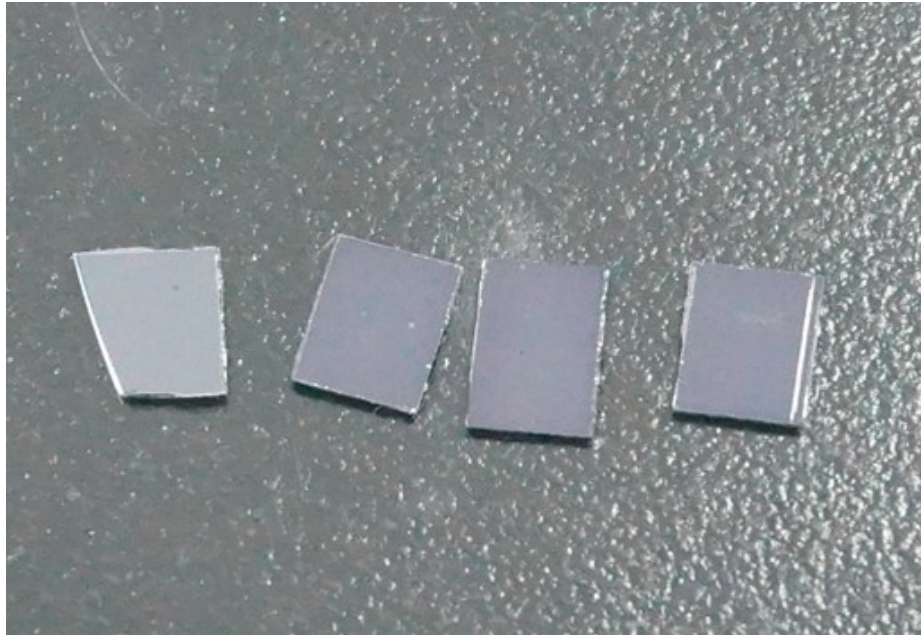

Figure. S3   Photographs of self-assembly substrates A to D after adding different amount of 0.1 M of Vc. A, 0.1 mL. B, 0.3 mL. C, 0.5 mL. D, 1.0 mL.

The effect of deposition time on the performance of SERS substrate. To investigate relationship between the self-assembly time of substrates and their SERS performance, substrates with different deposion time were prepared. Figure. S4 shows the Photographs of substrates a to d with deposition time of 0 min, 15 min, 30 min, 60 min in sequence. Figure. S5 are the correspongding optical images. Figure. S6 are the corresponding SERS spectrums of R6G. All these data exhibit clearly that the density of AgNPs on SERS substrate increase fast with self-assembly time within 1 h.
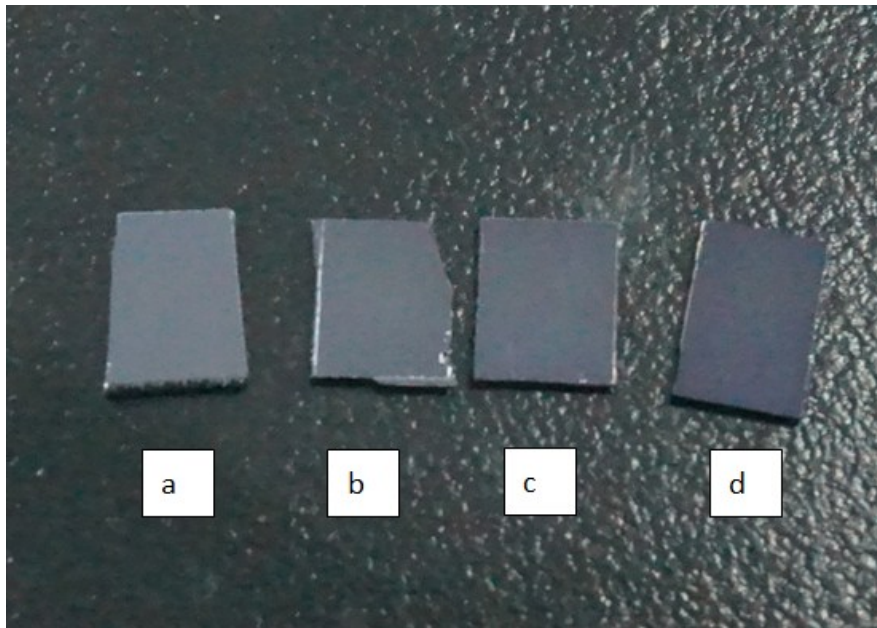
Figure. S4　Photographs of substrates a to d with different deposition time. (a) 0 min. (b) 15 min. (c) 30 min. (d) 60 min.
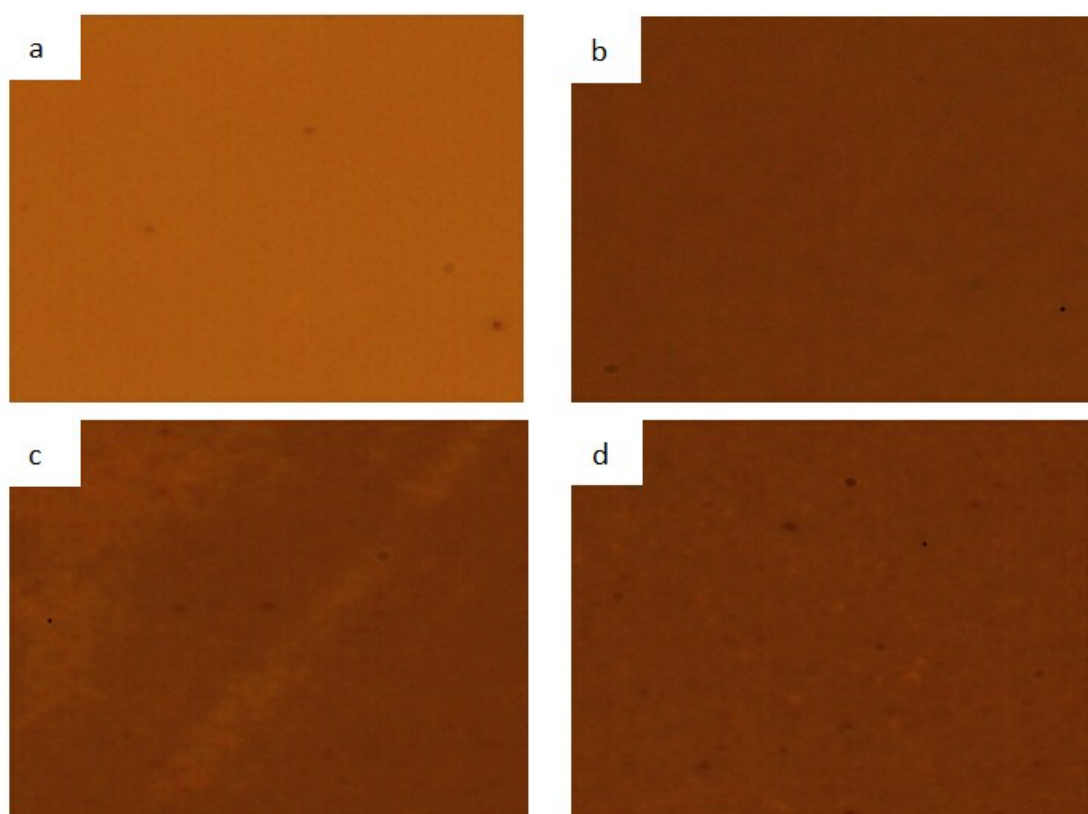
Figure. S5 Optical images of self-assembly substrates a to d with different deposition time. (a) 0 min. (b) 15 min. (c) 30 min. (d) 60 min.
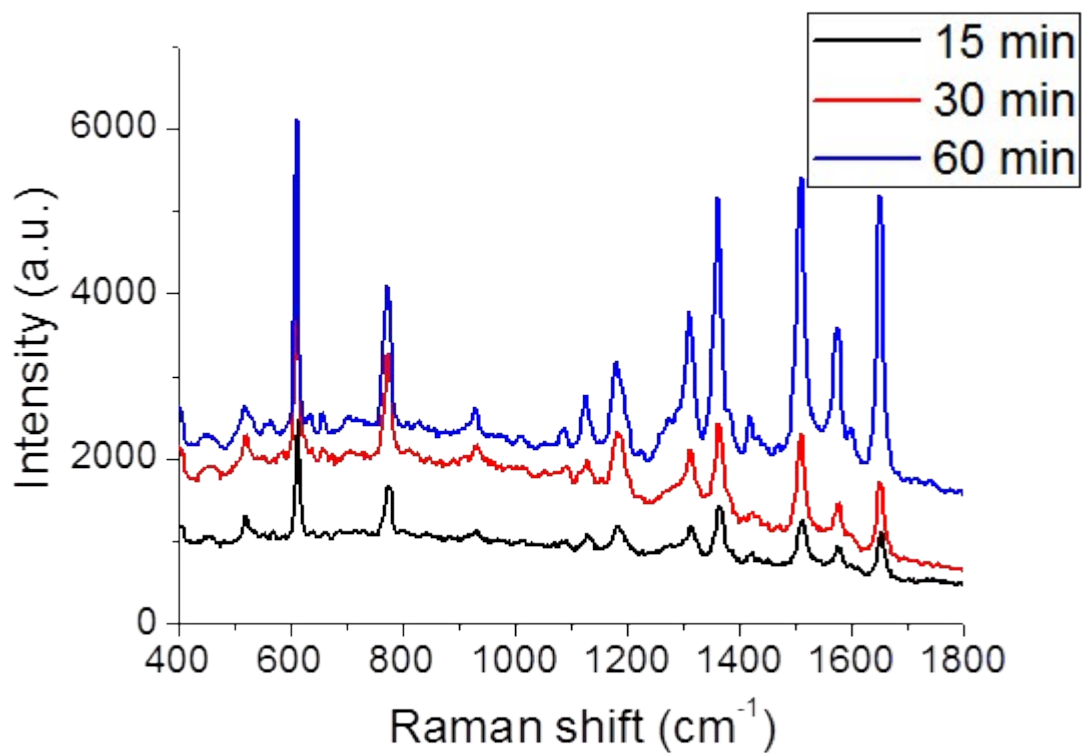
Figure. S6   SERS spectral comparison of 10^{-7} M R6G with different self-assembly time under 532 nm excitation (laser power: 0.025 mW, exposure time: 5 s).
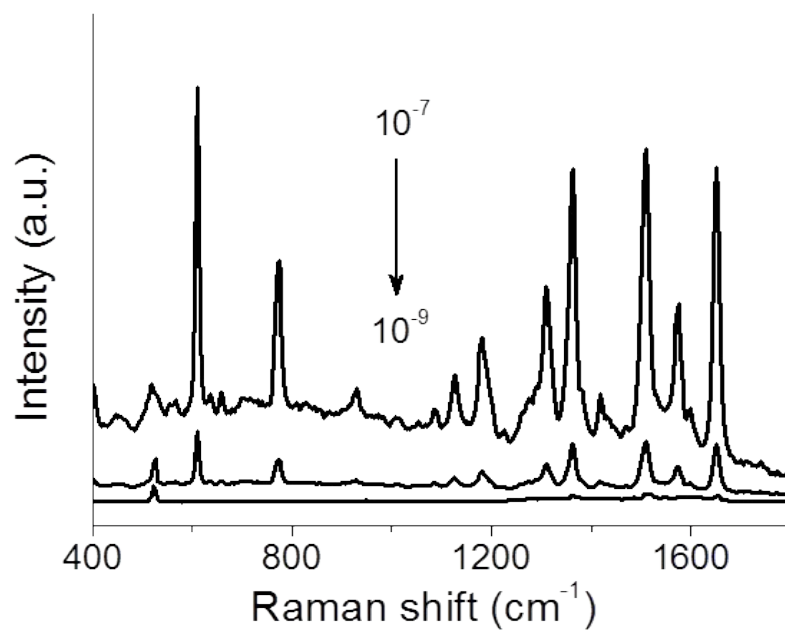
Fig. S7 SERS spectrums of R6G solutions at different concentrations under 532 nm excitation. From top to bottom: 10^{-7}, 10^{-8}, 10^{-9} M.

To calculate the enhancement factor (EF) of the best as-prepared substrate (i.e., substrate C), Regular Raman spectrum of 10^{-3} M R6G on silicon wafer and SERS spectrum of 10^{-7} R6G on C were measured. As shown in Figure. S8, the calculated EF is 3.65×10^8, indicating that the as-prepared substrate has excellent SERS performance.
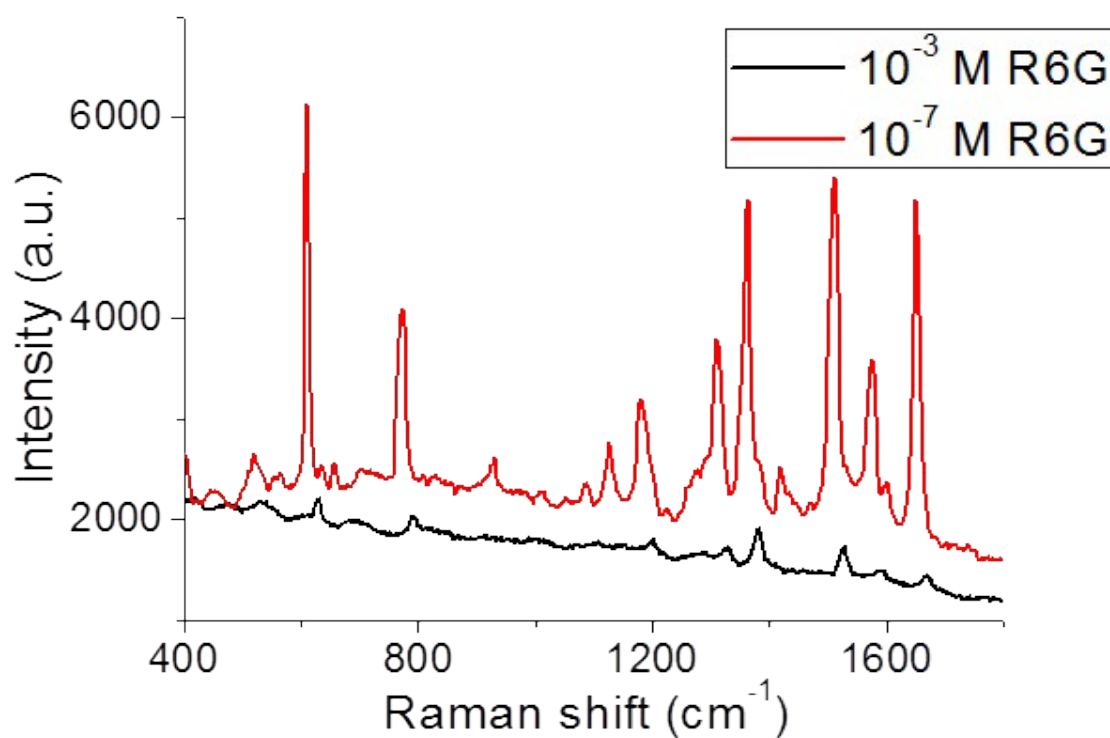

Figure. S8 Regular Raman spectrum of 10^{-3} M R6G and SERS spectrum of 10^{-7} R6G

To test the reproducibility of the substrate, SERS spectrums of R6G molecules with a concentration of 10^{-7} M from ten random-selected places on self-assembly AgNPs arrays were collected with laser of 532 nm under identical experimental conditions. The testing results are shown in Fig. S9. The relative standard deviation (RSD) of substrate C at 1365 cm^{-1} is about 8% , which indicates that our best as-prepared SERS substrate has a good reproducibility.
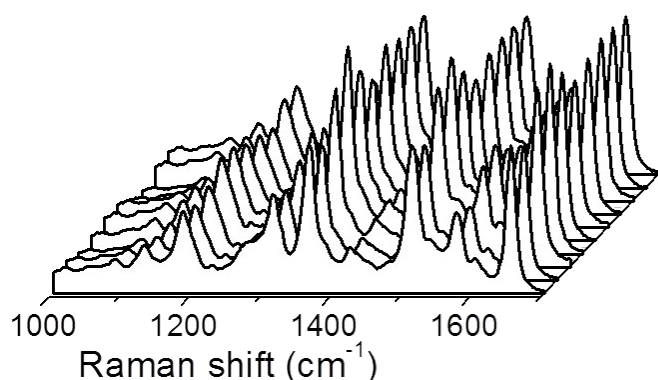

Fig. S9 SERS spectrums of R6G on substrate C from 10 randomly selected places under 532 nm excitation.

Reference

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2. M. V. Canamares, J. V. Garcia-Ramos, J. D. Gomez-Varga, C. Domingo and S. Sanchez-Cortes, *Langmuir* 2005 **21**, 8546-8553.
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4. G. F. S. Andrade, M. Fan and A. G. Brolo, *Biosensors & Bioelectronics*, 2010, **25**, 2270-2275.