Electronic Supplementary Material (ESI) for Nanoscale.

Surface-enhanced Raman scattering induced by the coupling of guided mode with localized surface plasmon resonances

(Supporting information)

Shaoying Wu[a,b], Yang Shen*[a] and Chongjun Jin*[a]

[a]State Key Laboratory of Optoelectronic Materials and Technologies, School of Materials Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China.
Email: jinchjun@mail.sysu.edu.cn
Email: sheny@mail2.sysu.edu.cn

[b]School of Electronics and Information Technology, Sun Yat-sen University, Guangzhou 510275, China

1. Simulation setting

FDTD Solutions (8.20.1634, Lumerical) was used to numerically simulate the optical properties of GNRs-GDMS. In the simulations, the refractive index of PS and quartz were set to be 1.59 and 1.48. The dielectric function of gold was described by a Drude model (dielectric permittivity ε_∞: 9.8, plasmon resonance: 1.37×10^{16} rad/s, plasma collision: 7.536×10^{14} rad/s).

The periodic and PML boundary conditions were applied in *x*-*y* plane and z direction, respectively. A plane wave source with a wavelength range from 400 nm to 1000 nm was used to excite the samples. As for the mesh override region covering the gold nanorods array, the mesh size in all the directions were 4 nm.

For the random GNRs array, the locations and directions of these GNRs were generated by a built-in random algorithm. Each GNR was regarded as a cylinder with a length of 75 nm and a radius of 16 nm based on the SEM image. In the simulations, the GNRs shared the same dielectric function with the gold mirror.

2. Random effect of GNRs arrangement

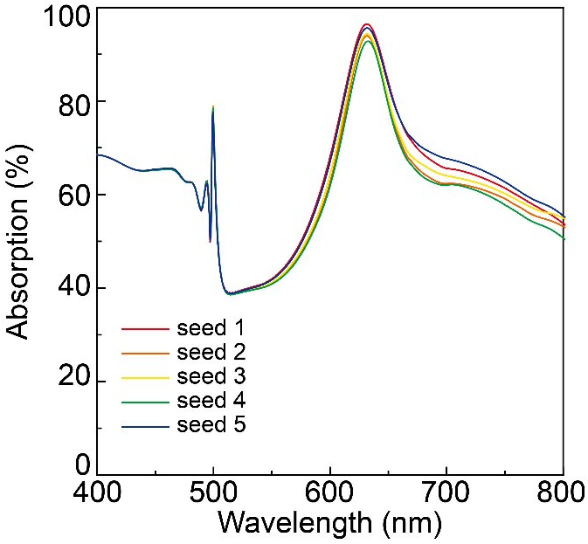

Figure S1. Simulated absorption spectra of the GNRs-GDMS with different arrangement of GNRs. The randomly-arranged GNRs arrays are generated by different random seeds. For all the simulations, the geometric parameters of GDMS are set to be a = 500 nm, s = 160 nm, h = 200 nm, w = 167 nm, and t = 100 nm. Different random seeds make no distinct difference on the location of absorption peaks as well as the absorption intensity.

3. **Simulated cross-sectional electric and magnetic field intensity distributions of GNRs-GDMS**

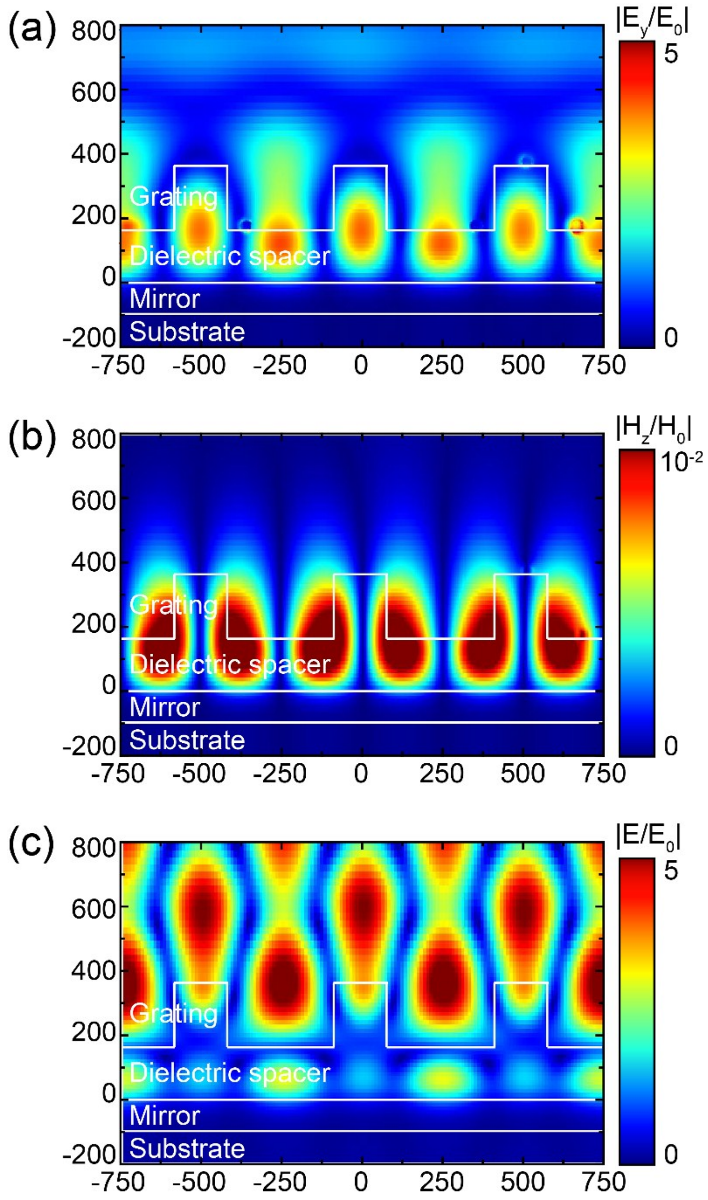

Figure S2. (a) Electric field intensity distribution in *y* direction of a GNRs-GDMS at 633 nm (b) Magnetic field intensity distribution in *z* direction of the GNRs-GDMS at 633 nm. (c) Total electric field intensity distribution of the GNRs-GDMS at 500 nm. The incident light has an electric field in *y* direction and a magnetic field in *x* direction. The geometric parameters of the GDMS are a = 500 nm, s = 160 nm, h = 200 nm, w = 167 nm, and t = 100 nm. The length and diameter of GNRs are l = 70 nm, d = 31 nm.

4. Simulated cross-sectional electric and magnetic field intensity distributions of GNRs-FPC

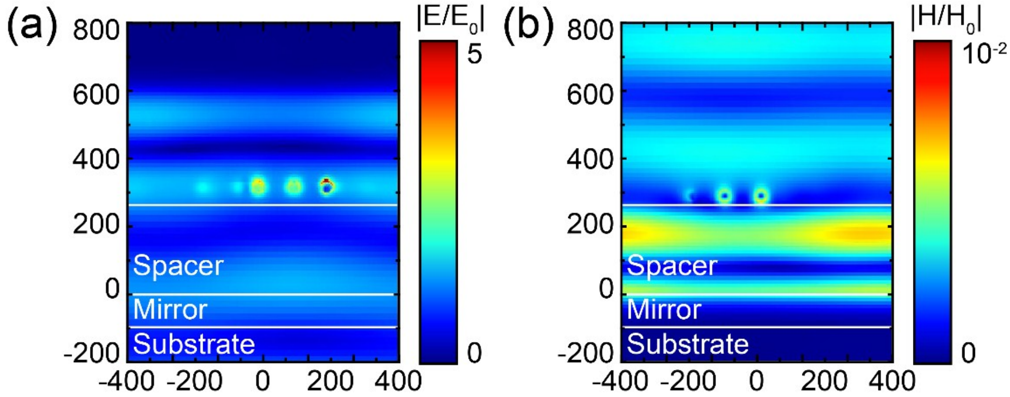

Figure S3. (a) Electric field intensity distribution of a GNRs-FPC at 633 nm. (b) Magnetic field intensity distribution of the GNRs-FPC at 633 nm. The thicknesses of the dielectric spacer and the mirror are set to be 270 nm and 100 nm, respectively, which ensure the resonance wavelength of the GNRs-FPC is 633 nm. The refractive index of the dielectric spacer is 1.59. The length and diameter of GNRs are set to be l = 70 nm, d = 31 nm, respectively.

5. Simulated cross-sectional electric and magnetic field intensity distributions of GNRs-DGS and the effect of mirror thickness on the transmission spectrum

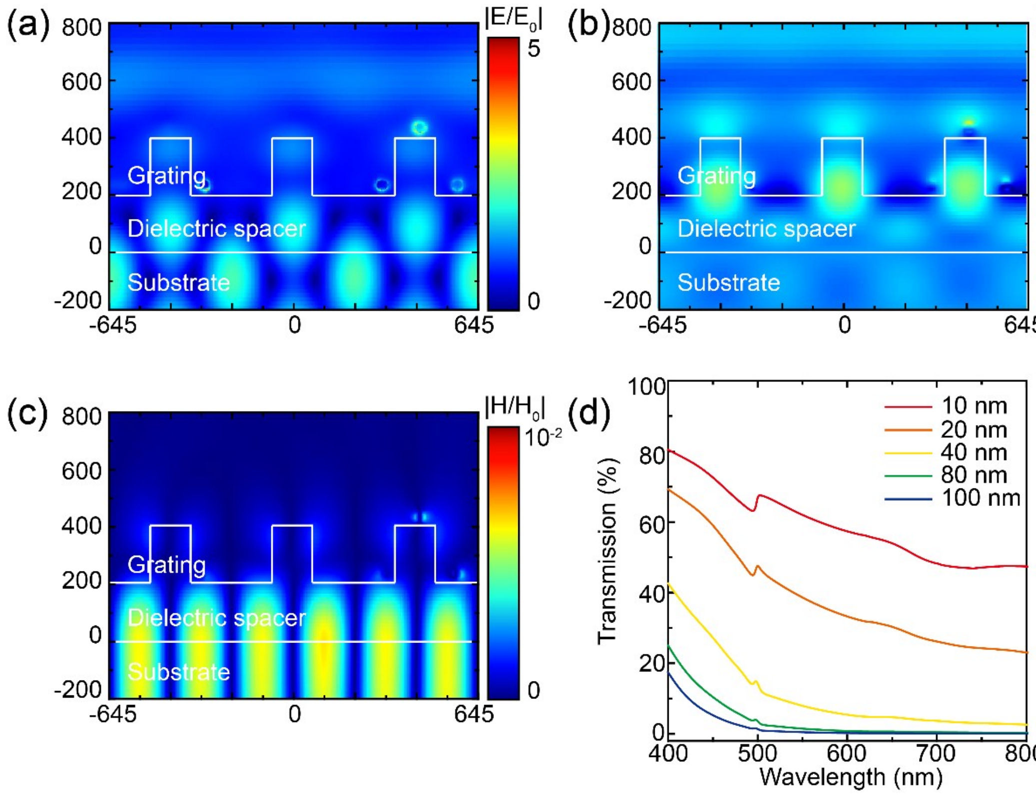

Figure S4 (a) Electric field intensity distribution in *y* direction of a GNRs-DGS at 633 nm. (b) Magnetic field distribution in *x* direction of the GNRs-DGS at 633 nm. (c) Magnetic field distribution in *z* direction of the GNRs-DGS at 633 nm. The incident light has an electric field in *y* direction and a magnetic field in *x* direction. The geometric parameters of DGS are a = 430 nm, s = 220 nm, h = 200 nm, w = 143 nm. The length and diameter of GNRs are l = 70 nm, d = 31 nm, respectively. (d) Simulated transmission spectra of the GNRs-GDMSs with different mirror thicknesses t (a = 500 nm, s = 160 nm, h = 200 nm, w = 167 nm). With the increase of t, the transmission of GNRs-GDMS showed a remarkable decrease, indicating that the energy leakage through the substrate has been effectively suppressed.

6. **Simulated absorption spectrum and cross-sectional electric field intensity distributions of a GNRs-GDMS when the light is polarized perpendicularly to the grating.**

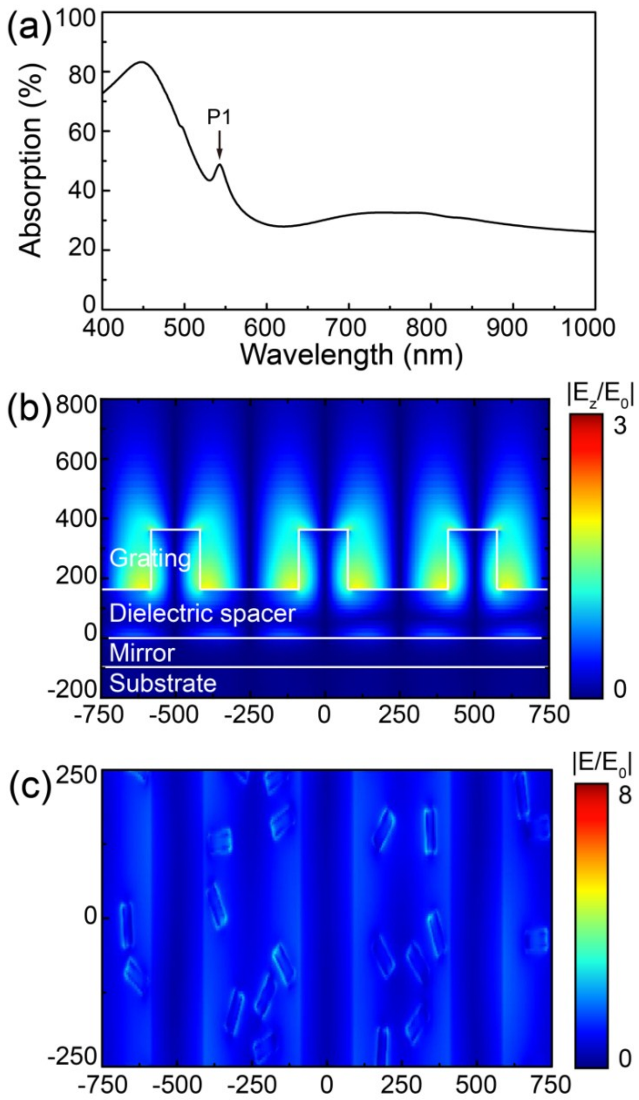

Figure S5 (a) Simulated absorption spectrum of a GNRs-GDMS (a = 500 nm, s = 160 nm, h = 200 nm, w = 167 nm) when the light is polarized perpendicularly to the grating. (b) Electric field intensity distribution in z direction of the GNRs-GDMS at 540 nm. (c) Electric field intensity distribution in x-y plane of the GNRs-GDMS at 540 nm. The location of the electric field distribution is 8 nm above the interface of PS and air in the groove.

7. **Absorption spectra of GDMS with different spacer thickness**

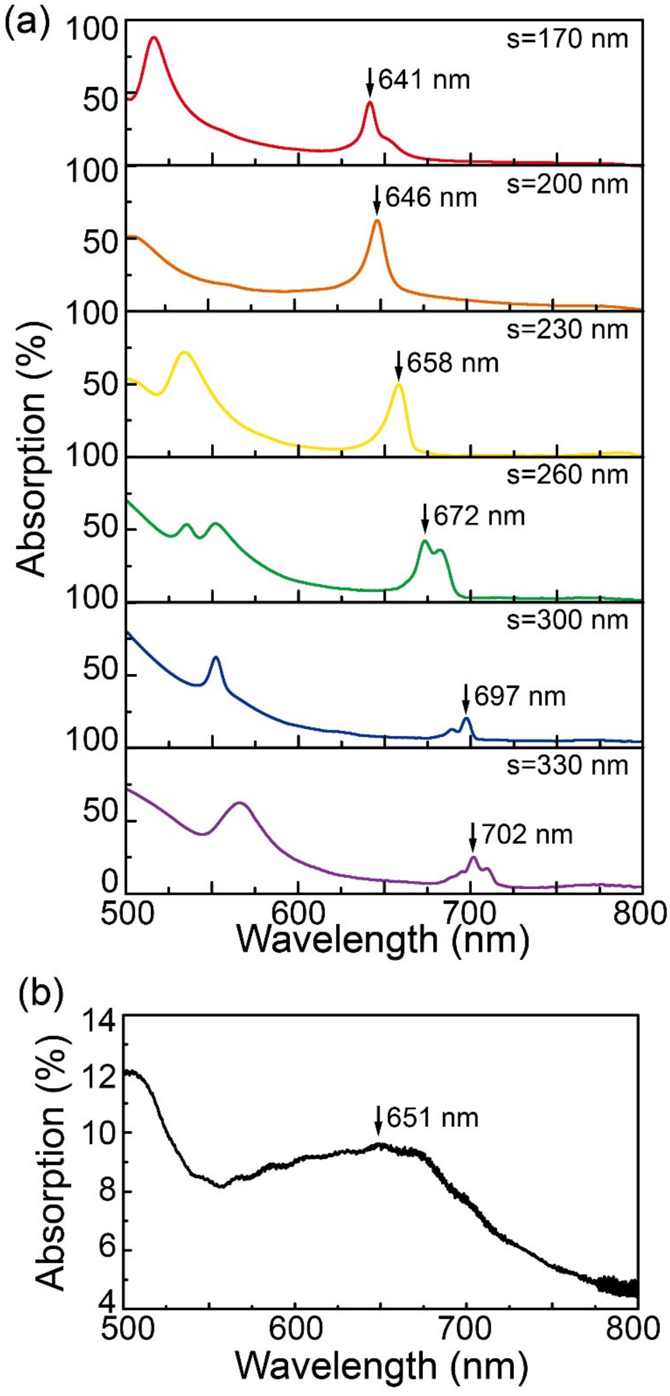

Figure S6. (a) Measured absorption spectra of the GDMSs with different spacer thicknesses *s* before the adsorption of GNRs. (b) Measured absorption spectrum of the GNRs adsorbed on a flat PS film.

8. Effect of spacer thickness on the absorption spectra of GNRs-GDMSs

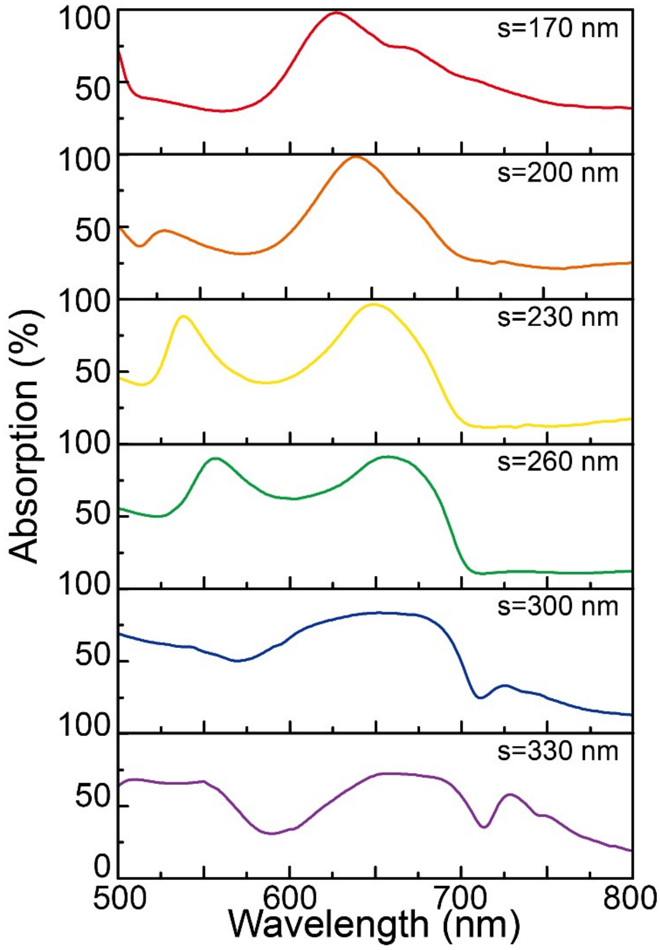

Figure S7. Simulated absorption spectra of the GNRs-GDMSs with different spacer thicknesses s. For all the simulations, the other geometric parameters of GDMS are a = 500 nm, h = 200 nm, w = 167 nm, and t = 100 nm. The length and diameter of GNRs are set to be l = 70 nm, d = 31 nm, respectively.

9. Effect of period and height of the grating on the absorption spectra of GNRs-GDMSs.

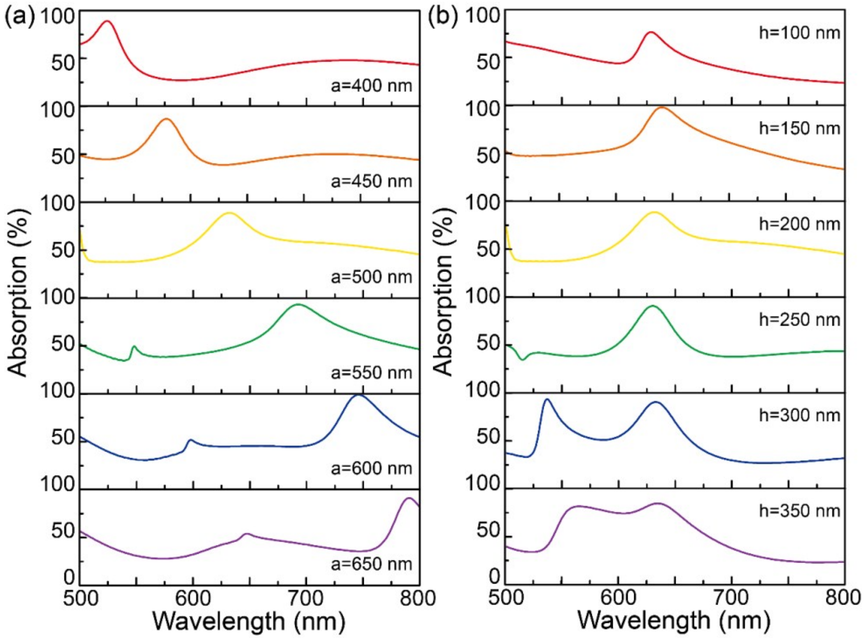

Figure S8. (a) Simulated absorption spectra of GNRs-GDMSs (h = 200 nm, t = 100 nm) with various grating periods from 400 to 650 nm. As a = 500 nm, the resonance wavelength of GNRs-GDMS matches the excitation laser line of 633 nm; (b) Simulated absorption spectra of GNRs-GDMSs (a = 500 nm, t = 100 nm) with various grating heights from 100 to 350 nm. When h is increased from 100 to 250 nm, the wavelength and intensity of the peak P1 (coupling between the LSPR and guided mode) remains unchanged. Considering that a high aspect ratio (deep groove) will reduce the yield, we chose a moderate grating height of 200 nm. In addition, as the grating height is further increased, a new absorption peak at shorter wavelength appears. This resonance is related to the high-order F-P modes.

10. EF calculations

In this work, the average EF of GNRs-GDMS was calculated by using the following expression:

$$EF = \frac{I_{SERS}}{I_{RS}} \times \frac{N_{RS}}{N_{SERS}} \times \frac{P_{RS}}{P_{SERS}} \times \frac{t_{RS}}{t_{SERS}} \tag{1}$$

where *I*, *N*, *P and t* correspond to the Raman intensity, total number of probed molecules, laser power and acquisition time in SERS and RS measurements, respectively. Here, we measured the RS spectrum of a R6G solution (10^{-3} M) and SERS spectrum of a GNRs-GDMS sample treated by a R6G solution (10^{-7} M), as shown in following Figure S9. For example, at 1649 cm^{-1}, I_{SERS}, P_{SERS} and t_{SERS} are 5543, 0.6 mW and 10 s, respectively. While I_{RS}, P_{RS} and t_{RS} are 53, 30 mW and 30 s, respectively. N_{SERS} and N_{RS} can be calculated from the following equations,

$$N_{RS} = c_{RS} S h \tag{2}$$

$$N_{SERS} = [(\pi dl/2)/S_{R6G}]\eta NS \tag{3}$$

where c_{RS} (10^{-3} M) is the concentration of the R6G solution used in the normal Raman measurement, *S* is the laser spot area (3.14 μm^2), and *h* (60 μm) is the height of the solution drop, which is sandwiched by a silicon substrate and a coverslip. Therefore, N_{RS} is determined to be 1.13×10^{8}. For N_{SERS}, the GNRs are considered as cylinders with a diameter *d* of 31 nm and a length *l* of 75 nm in the calculation, and its superficial area is $\pi dl/2$ (only the upper half part is in view). S_{R6G} is the footprint of R6G molecule, which is approximately to be 4 nm^2 [1], and η (0.907) is the duty ratio for the hexagonal close-packed arrangement of R6G molecules on the GNRs surface. Here, the adsorbed R6G molecule is considered as a monolayer when the GNRs-GDMS was treated by the R6G aqueous solution with a concentration of 10^{-7} M[1]. The density of GNRs *N* is about 376 nanorods/μm^2 obtained from the top-view SEM image. N_{SERS} is therefore determined to be 9.8×10^{5}. According to Equation (1), the average EF is calculated to be 1.84×10^{6} at 1649 cm^{-1} for the 10^{-7} M R6G as the analyte.

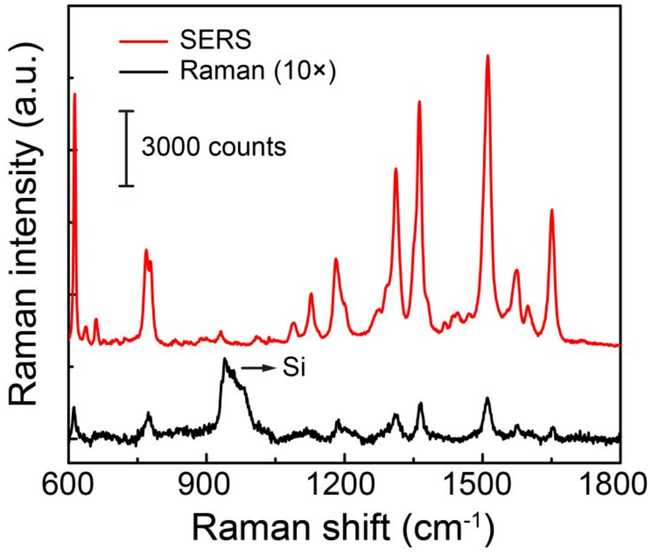

Figure S9. Raman spectrum of a GNRs-GDMS (a = 500 nm, h = 200 nm, s = 200 nm, t = 100 nm) treated by a R6G solution with a concentration of 10^{-7} M (red curve) and Raman spectrum of a R6G solution with a concentration of 10^{-3} M (10×, black curve).

The calculated EFs at the main peaks of 614, 775, 1313, 1361, 1512 and 1649 cm^{-1} are shown in Table S1 as follow.

Table S1. Enhancement factors for a GNRs-GDMS at 614, 775, 1313, 1361, 1512 and 1649 cm^{-1} peaks.

Peak position (cm^{-1})	614	775	1313	1361	1512	1649
Raman intensity	127	110	99	152	177	53
SERS intensity	10297	7942	7351	10083	11999	5543
EF	1.41×10^{6}	1.26×10^{6}	1.29×10^{6}	1.15×10^{6}	1.18×10^{6}	1.82×10^{6}

11. Details about the home-made micro-area optical measurement system

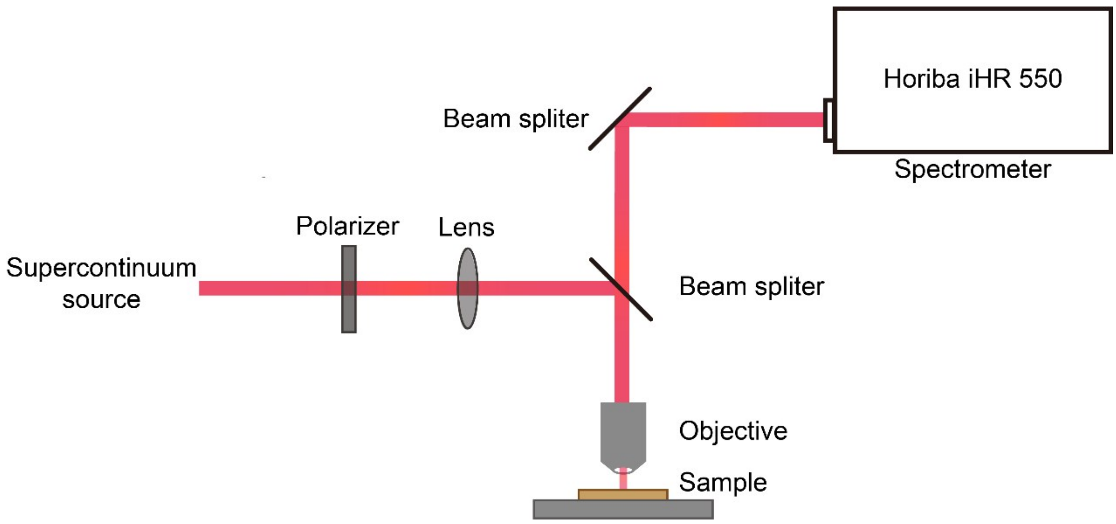

Figure S10. Scheme of the home-made micro-area optical measurement system. A white-light supercontinuum source (Super K, NKT Photonics) was polarized by a Glan-Taylor prism and collimated by a lens and 100×objective (Olympus MPlan FL N, NA 0.9) to generate a quasi-parallel light with the beam spot of 2 μm in diameter. This beam was illuminated on the sample and the reflected light was collected by the same objective and finally coupled to a spectrometer (iHR550, Horiba). The spectra were corrected by the reflection spectrum of a standard silver mirror.

Reference:

[1] Q. Fu, Z. Zhan, J. Dou, X. Zheng, R. Xu, M. Wu, Y. Lei, *ACS Appl. Mater. Interfaces*, 2015, **7**, 13322-13328.