Indocyanine green-loaded gold nanostars for sensitive SERS imaging and subcellular monitoring of photothermal therapy

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Enhancement Factor (EF) Calculation

To calculate the EF of GNS-ICG-BSA SERS nanotags, a 10^{-2} M of ICG solution is used for normal Raman detection, and 10 μL of GNS-ICG-BSA solution with the adsorbed ICG concentration of 10^{-4} M is used for SERS detection.

The most widely used definition for EF is[1]

$$EF = \frac{I_{surf}}{I_{bulk}} \times \frac{N_{bulk}}{N_{surf}}$$

where I_{surf} and I_{bulk} are the integrated intensities of ICG molecules adsorbed on GNS-ICG-BSA SERS nanoprobes and from 10^{-2} M of ICG bulk solution, respectively. N_{surf} and N_{bulk} are the corresponding numbers of ICG molecules adsorbed on GNS-ICG-BSA SERS nanoprobes and in the bulk solution effectively illuminated by the laser beam, respectively.

$$N_{bulk} = Ahc_{bulk}N_A$$

where A is the area of the laser focal spot, h is the confocal depth of the laser, and h is 13 μm according to our previous work,[2] c_{bulk} is the concentration of ICG bulk

solution, here c_{bulk}=10^{-2} M, N_A is the Avogadro constant.

$$N_{surf} = \frac{c_{surf} v N_A A}{\pi r^2}$$

where c_{surf} is the concentration of ICG molecules adsorbed on GNS-ICG-BSA SERS nanoprobes, here c_{surf}=10^{-4} M. v is the volume of ICG solution contained in 10 μL of GNS-ICG-BSA solution. According to the procedure 2.2 in the manuscript, the ratio of ICG reporter solution to GNS-ICG-BSA solution is 0.03, so here v is 0.3 μL. r is the radius of 10 μL of GNS-ICG-BSA solution formed on the silicon substrate, r=3.5 mm.

Figure S1a, S1b are the normal Raman spectrum of 10^{-2} M ICG solution and SERS spectrum of 10^{-4} M GNS-ICG-BSA solution, respectively. The integrated intensities of the bands for I_{bulk} (1431 cm^{-1}) and I_{surf} (1444 cm^{-1}) are 3089 and 373862 cps, respectively. Considering the different number of molecules in each unit volume for normal Raman spectrum and SERS spectrum acquisition,[2] I_{surf} / I_{bulk}=373862×10^2 / 3089.

Finally, the EF of GNS-ICG-BSA SERS nanoprobes can be calculated as 2.02×10^6.
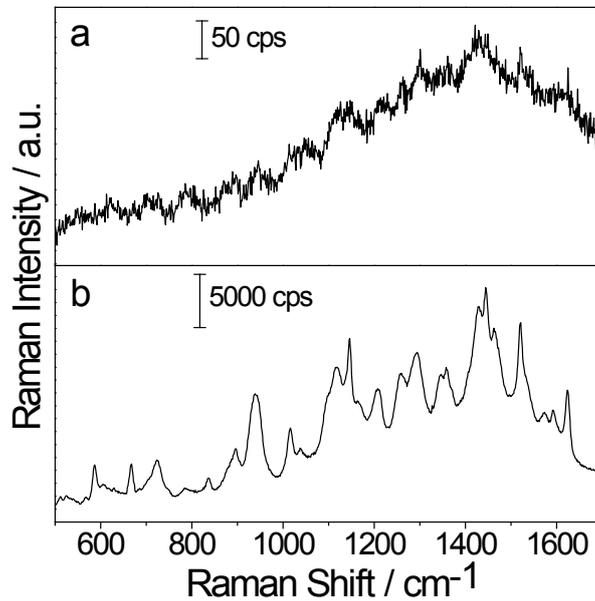
Figure S1 (a) Normal Raman spectrum of 10^{-2} M ICG solution. Laser power: 15.7 mW. (b) SERS spectrum of 10^{-4} M GNS-ICG-BSA solution. Laser power: 15.7 mW.
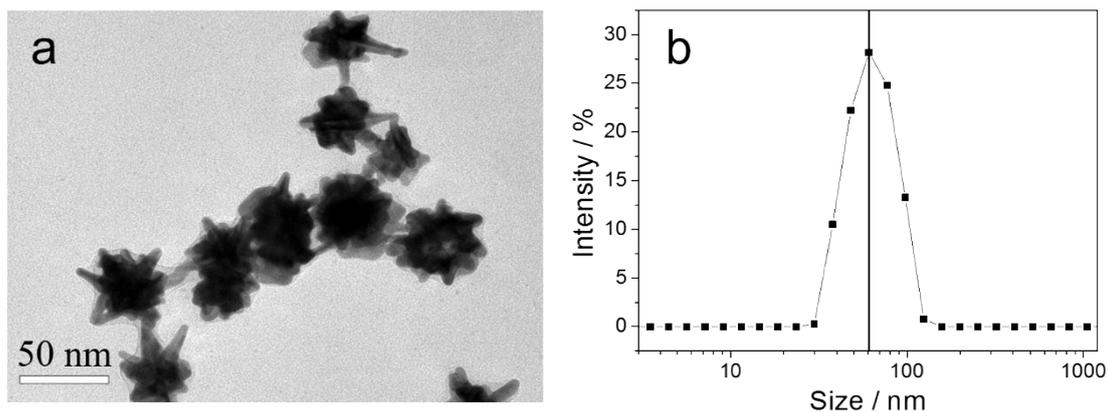
Figure S2 (a) TEM image and (b) size distribution of GNS-ICG-BSA nanoprobe after laser irradiation (808 nm, 3.0 W/cm^2) for 7 min.
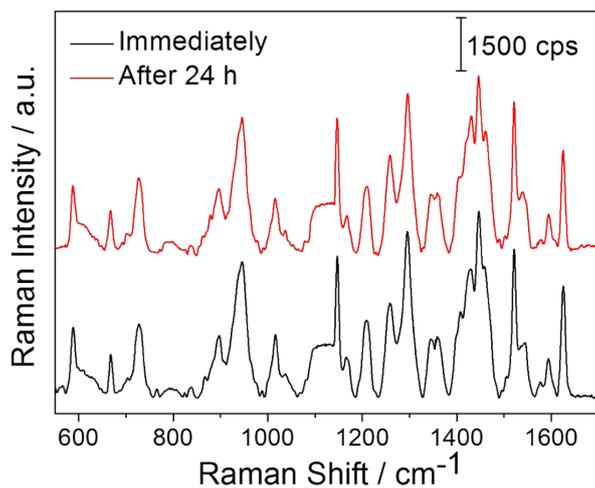
Figure S3 GNS-ICG-BSA nanotags were heated to 45 ^{o}C by 808 nm laser (1.0 W/cm^2), and the SERS spectra were acquired immediately and after the storage at room temperature for 24 h, respectively.
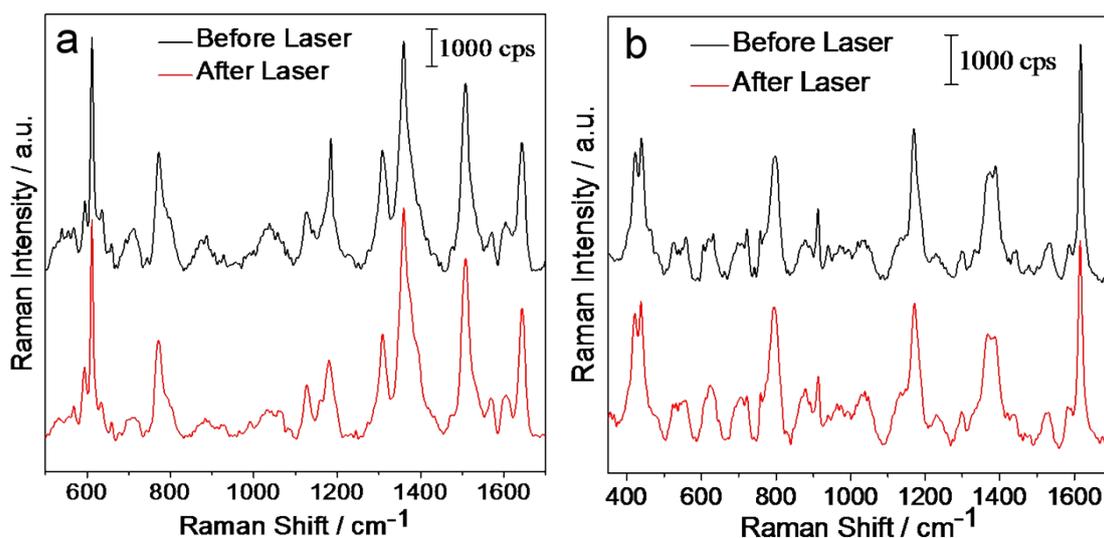
Figure S4 The SERS spectra of (a) GNS-R6G-BSA and (b) GNS-CV-BSA nanotags without and with 808 nm laser irradiation.
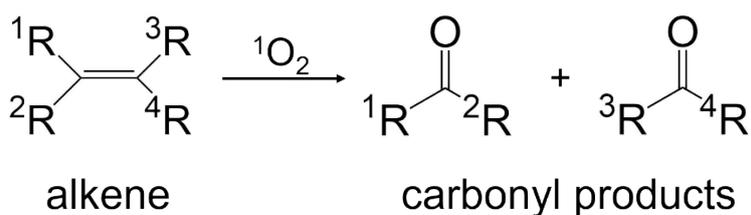
Scheme S1 Schematic diagram of ICG decomposition mechanism upon laser irradiation. An alkene (double bond in a polymethine chain) with a general structure is shown, and ^{1}R to ^{4}R represent different functional groups.

References

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