Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B

Supporting Information

Self-focusing Au@SiO_2 nanorods with rhodamine 6G as highly sensitive SERS substrate for carcinoembryonic antigen detection

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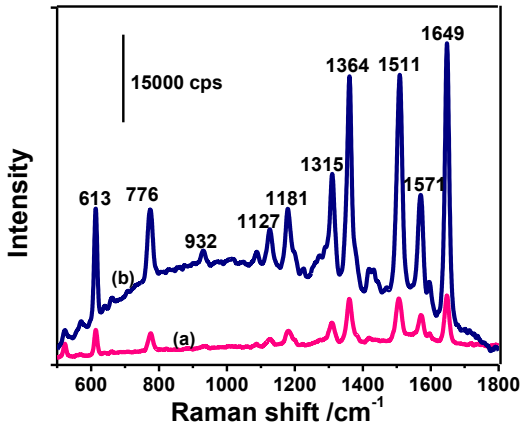

Fig. S1 Raman spectra of 10^{-8} M R6G on (a) Au@SiO_2 NPs (~40 nm core/ with shell 1-2 nm),[1] and (b) Au@SiO_2 NRs (~70 nm core/ with shell 1-2 nm), respectively.

The enhancement factors for SERS activity were calculated from the equation $EF = \frac{(I_{SERS}/C_{SERS})}{(I_{ref}/C_{ref})}$, taken from reference.[2] In this equation, C_{ref} (10^{-1} M) and C_{SERS} represent the concentrations of R6G on the silicon substrate and R6G on Au@SiO_2 NRs substrate used for obtaining the I_{ref} and I_{SERS}, respectively, in measurements.

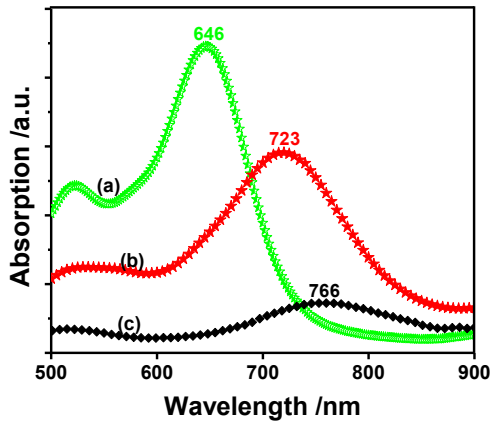

Fig. S2 UV-vis spectra of Au nanorods in different lengths: (a) 47 nm; (b) 70 nm; and (c) 82 nm

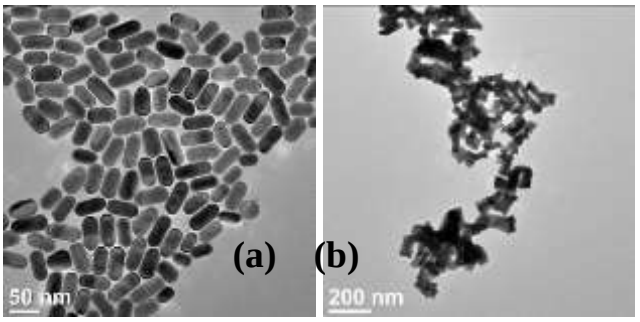

Fig. S3 TEM images of (a – b) Au nanorods (~47 nm, and ~82 nm with 15 μL, and 8 μL of Au seed solution), respectively.

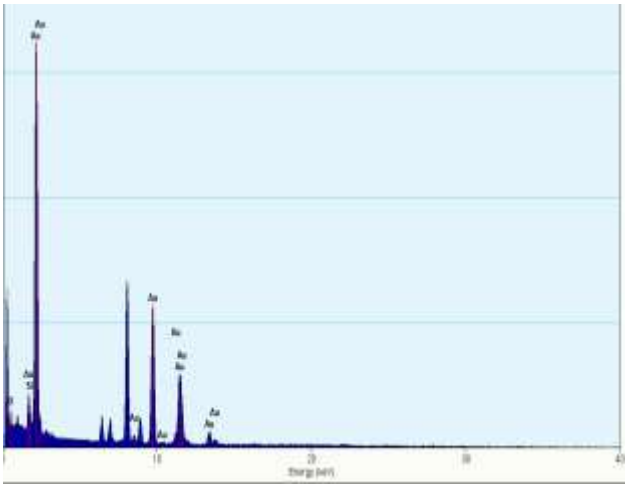

Fig. S4 EDX of Au@SiO_2 core/shell nanorods (~70 nm core/ with shell 1-2 nm)

Fig. S5 collects three sets of XRD patterns of Au NRs, and Au@SiO_2 NRs. In general, SiO_2 shows a broad amorphous feature at 2θ (44° - 77.74°) – see Fig. S5(b), and Au peaks appear at 2θ 38°,44°, 65°, and 78°, corresponding to gold (111), (200), (220), and (311), respectively as shown in Fig. S5(a). These peaks are consistent with the Joint Committee on Powder Diffraction Standard (JCPDS 04-0784). The Au peaks become sharper with the growth of Au nanorods. On the other hand, SiO_2 maintains its amorphous phase, and the formation of new phases is not detected.

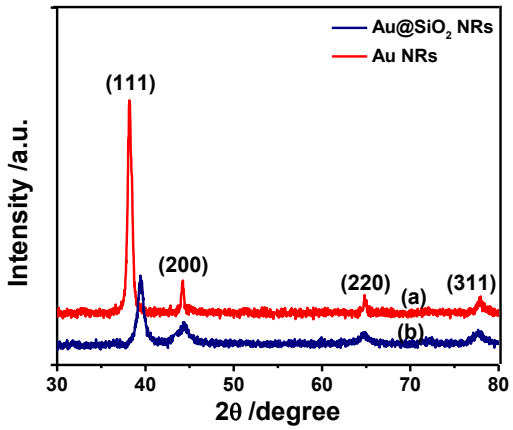

Fig. S5 XRD patterns of (a) Au NRs (~70 nm), and (b) Au@SiO_2 NRs (~70 nm core/ with shell 1-2 nm).

Fig. S6 shows SEM images of Au@SiO_2 NRs without CEA (before) and in the presence of CEA (after). Moreover, the inter-particle distances between two neighboring nanorods have been calculated to show how the CEA concentration significantly affects the SERS enhancement due to the "self-focusing" structure and different inter-particle distances. Fig. S7 shows the dependence of the self-focusing structure on the mean inter-particle distance and Raman intensity using Au@SiO_2 NRs (~70 nm core/ shell 1-2 nm) in the presence of various CEA antigen concentrations at 0 pg mL^{-1}, 1 pg mL^{-1}, and 100 pg mL^{-1}, respectively. When the CEA concentration increases, the distance between two particles becomes shorter, and the SERS signal intensity gets significantly higher. As shown in Fig. S8, the distribution of CEA antigens on Au@SiO_2 NRs carrying R6G and antibody (scan area: 20 × 20 μm^2) is illustrated based on the highest signal intensity of peak at 1619 cm^{-1}. It should be noted that the uniform distribution of the R6G characteristic peak signals represented uniform CEA antigen-antibody distribution on the Au@SiO_2 NRs substrate in this wavenumber region can be attributed to the self-focusing structures that greatly enhanced the reliability of the measurements, as seen in the SERS mapping, Fig. S8.

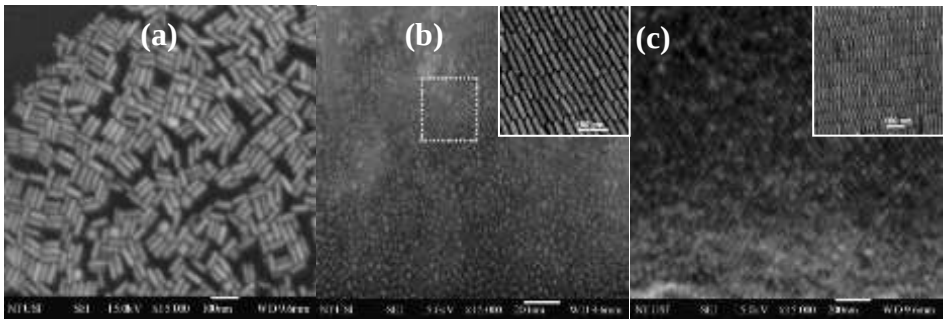

Fig. S6 SEM images of Au@SiO_2 NRs (~70 nm core/ shell 1-2 nm) in the presence of (a) 0 pg mL^{-1}, (b) 1 pg mL^{-1} and (c) 100 pg mL^{-1} CEA antigen concentration, and HRSEM images are also displayed as inserts, respectively.

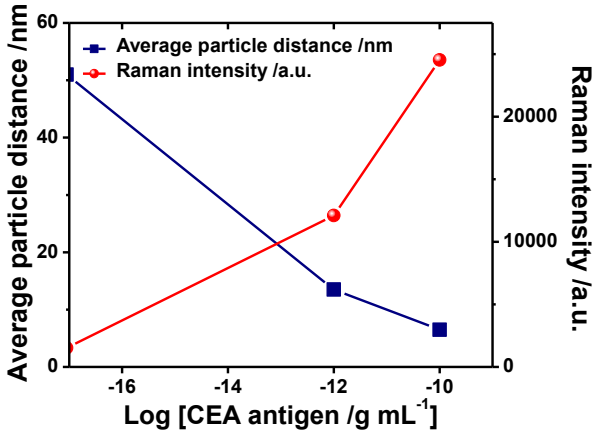

Fig. S7 Shows the self-assemble structure via the relative distance between particles and Raman intensity using Au@SiO_2 NRs substrate (~70 nm core/ shell 1-2 nm) in the presence of various CEA antigen concentrations at 0 pg mL^{-1}, 1 pg mL^{-1}, and 100 pg mL^{-1}, respectively. Each data point represents the mean value of ten distance measurements (i.e, the end-to-end distance between two particles) and average Raman intensity from three spectra.

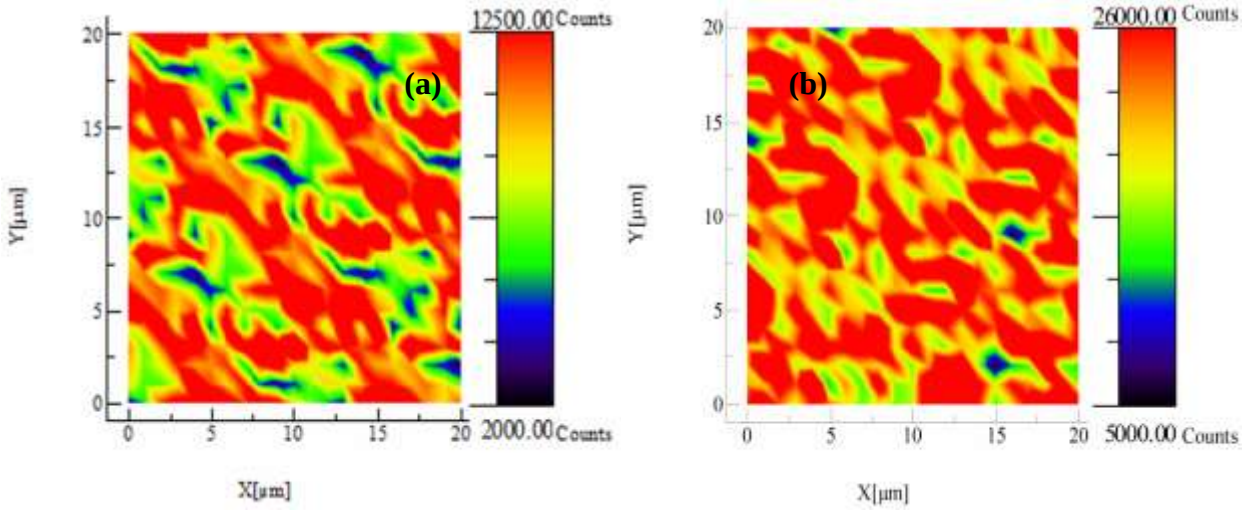

Fig. S8 SERS mapping of (a) 1 pg mL^{-1} and (b) 100 pg mL^{-1} CEA antigen on Au@SiO_2 NRs/R6G-conjugated with antibody after formation of self-focusing structures via the antibody-antigen interactions between Au@SiO_2 NRs based on signal of peak at 1619 cm^{-1}. This image is a 2D projection (scan area 20 × 20 μm^2), respectively.

References

1 T. T. B. Quyen, W.-N. Su, K.-J. Chen, C.-J. Pan, J. Rick, C.-C. Chang and B.-J. Hwang, *J. Raman Spectrosc.* **2013**, DOI 10.1002/jrs.4400

2 E. C. Le Ru, E. Blackie, M. Meyer and P. G. Etchegoin, *J. Phys. Chem. C*, 2007, **111**, 13794-13803.