Supporting Information for

"Preparation and Evaluation of Nanocellulose-Gold Nanoparticle Nanocomposites for SERS Applications"

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SI contains photos and SEM images of the AuNP/BC samples, detailed Raman spectrum of blank AuNP/BC sample and AuNP/BC+MGITC with different drying time. It also includes the Raman image of AuNP/BC+R6G (low concentration) and the SEM image of AuNP-ps/BC.

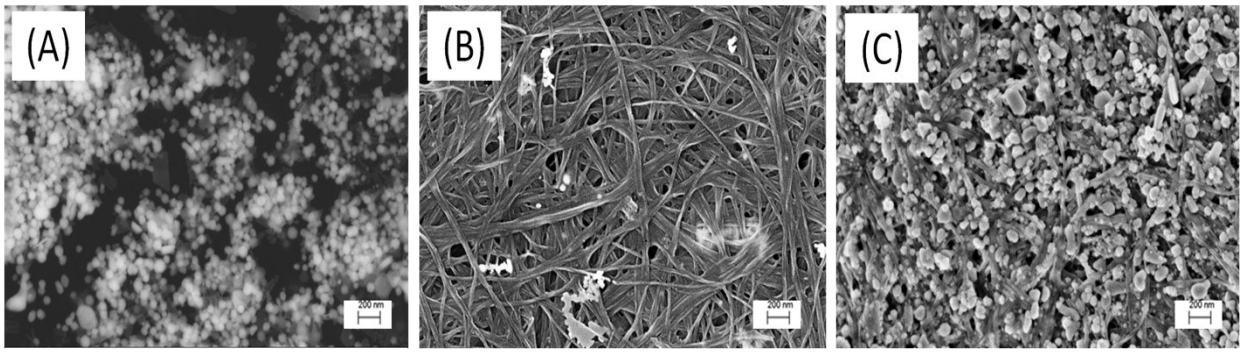

Figure S-1. SEM images of AuNP/BC prepared by A) Na_3Cit reduction at room temperature, B) BC surface hydroxyl group reduction at 373 K, and C) Na_3Cit reduction at 373 K.

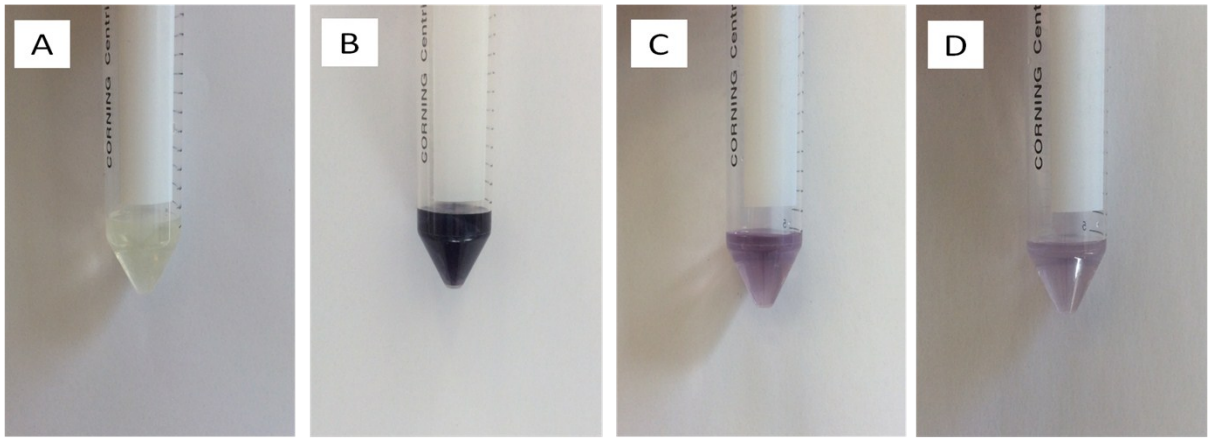

Figure S-2. Residual AuNPs following immersion of BC in $HAuCl_4$ (1 mM) and Na_3citrate (3 mM) solution for A) 0 h, B) 4 h, C) 48 h, and D) 72 h. (In each case the BC hydrogel was removed from the tube prior to taking the picture.)

Adsorption of preformed AuNPs by BC

Methods. Pre-synthesized AuNPs (AuNP-ps) with a uniform size of 50 nm were synthesized using the seed-mediated growth method.[1, 2] A piece of BC hydrogel (2 cm^2) was immersed in 15 mL of AuNP-ps suspension (5.35×10^{10} NPs/ml) and shaken for 24 h. The UV-Vis spectra of the AuNP-ps suspension before and after adsorption were measured to quantify the adsorption capacity of BC for AuNP-ps. If all AuNP-ps were adsorbed by BC (no LSPR band in the UV-vis spectrum), the hydrogel was immersed in a second 15 mL of AuNP-ps suspension. This process was repeated for four cycles until a detectable AuNP LSPR band appeared in the UV-vis spectrum, thus indicating the adsorption process had reached saturation. The concentration of AuNPs remaining in suspension was calculated by dividing the LSPR band height of the AuNP-ps suspension prior to the sorption experiment by that after sorption.

Results. We hypothesized that preformed AuNPs of uniform size could be integrated into the 3D BC structure to meet various application requirements. To test this, we conducted an experiment to load pre-synthesized AuNPs (AuNP-ps) into a BC substrate and evaluate the adsorption capacity of BC for AuNP-ps. As shown in Fig. S-2, the UV-Vis spectrum of AuNP suspensions before (Fig. S-2A) and after sorption by the BC exhibited a single peak at 533 nm, which corresponds to the LSPR band of the 50 nm AuNPs. Following the first and second sorption cycles the UV-Vis spectra are straight lines, thus indicating complete removal of AuNP-ps by the BC (Fig. S-2B). After the third sorption cycle, 1.5% of the AuNP-ps remained in suspension. After the fourth sorption cycle, a prominent peak appeared at 533 nm (8.6% AuNP-ps remained), indicating complete surface saturation. Based upon this experiment the sorption capacity of BC for the AuNPs was calculated to be 5.82 (g AuNP/g BC). A SEM image of the final nanocomposite illustrates the incorporation of AuNP-ps within the BC matrix. Importantly, however, the AuNPs are not homogeneously distributed within the matrix and thus it was concluded that nanocomposites made by this approach would not exhibit reproducible SERS responses. Nonetheless, this result demonstrates that BC has a very large sorption capacity for AuNPs (about 6× its own weight) and by extension this is probably true for other nanostructures.

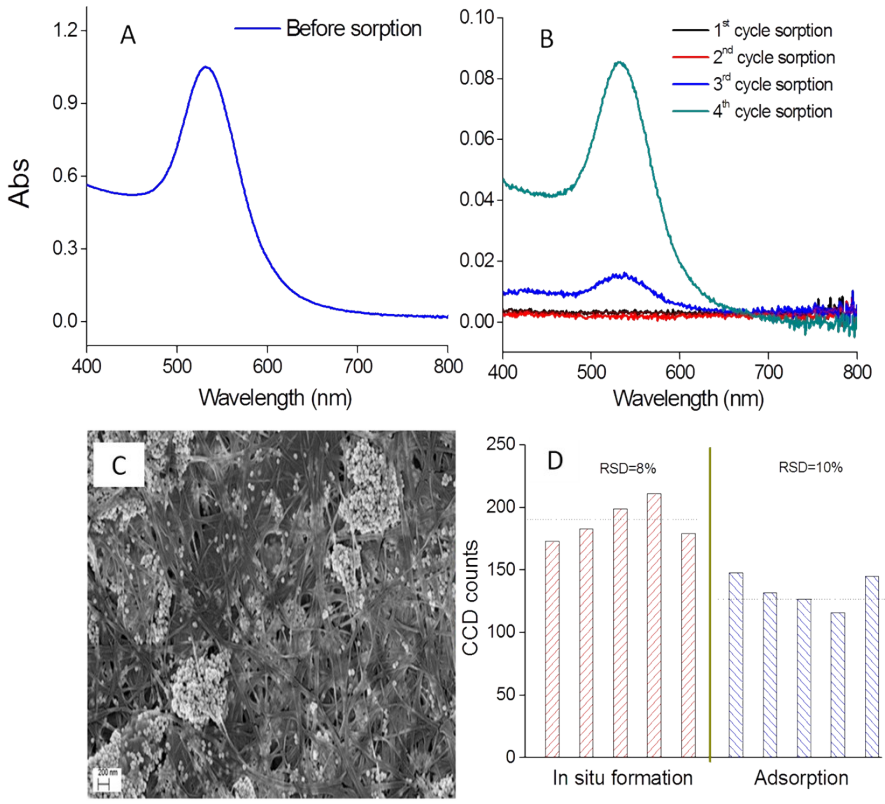

Figure S-3. Experimental evidence for AuNP-ps uptake by BC. A) Initial extinction spectrum of 50 nm AuNPs in suspension. B) Extinction spectra of AuNPs in suspension following exposure to BC. After three exposure cycles there is a measurable LSPR band thus indicating the BC is reaching its sorption capacity. C) SEM image illustrated the entrainment of AuNPs within the BC matrix. Note that the AuNPs are not homogeneously distributed within the matrix. D) SERS intensity of MGITC average spectra in five randomly selected areas of *in situ* synthesized AuNP/BC and AuNP/BC prepared by sorption of pre-formed AuNPs. (Dotted line is the average Raman intensity of the five average spectra.)

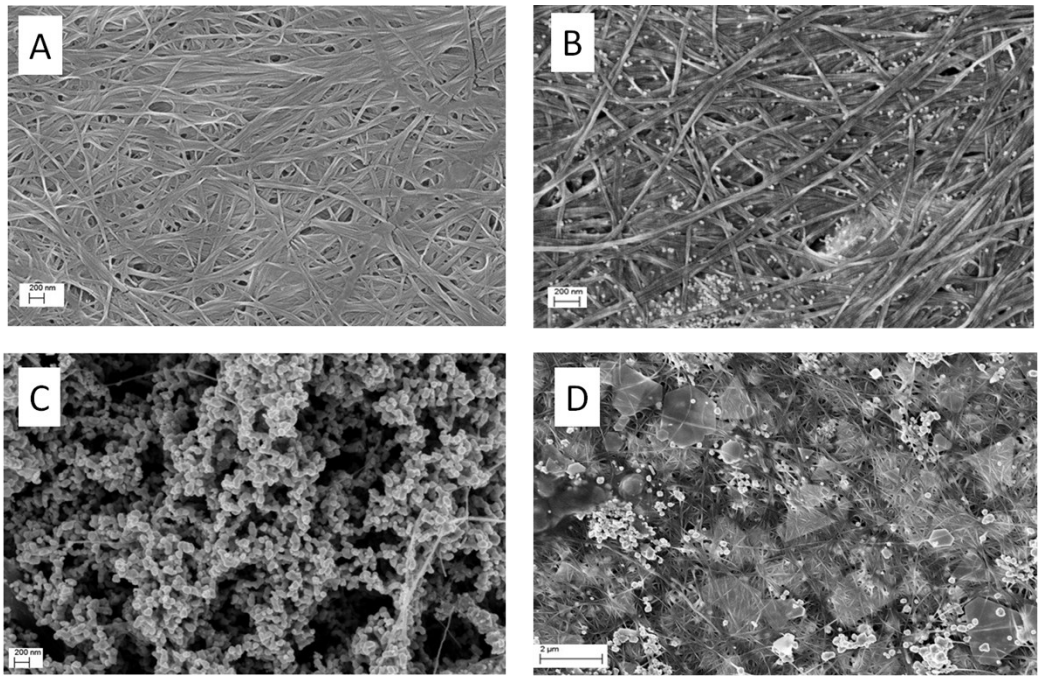

Figure S-4. Secondary electron images of A) BC alone, B) AuNP/BC-3-1, C) AuNP/BC-3-5, D) AuNP/BC-1-10.

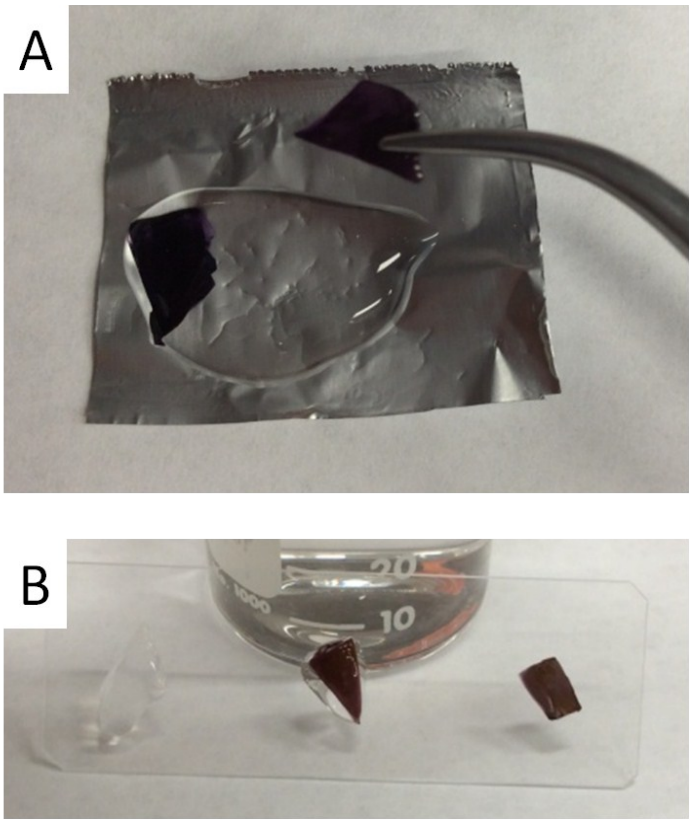

Figure S-5. A) AuNP/BC-3-8 bound to aluminum foil and peeled off when wetted. B) *left*: BC hydrogel, *middle*: AuNP/BC-1-10 hydrogel, and *right*: AuNP/BC-1-10 film.

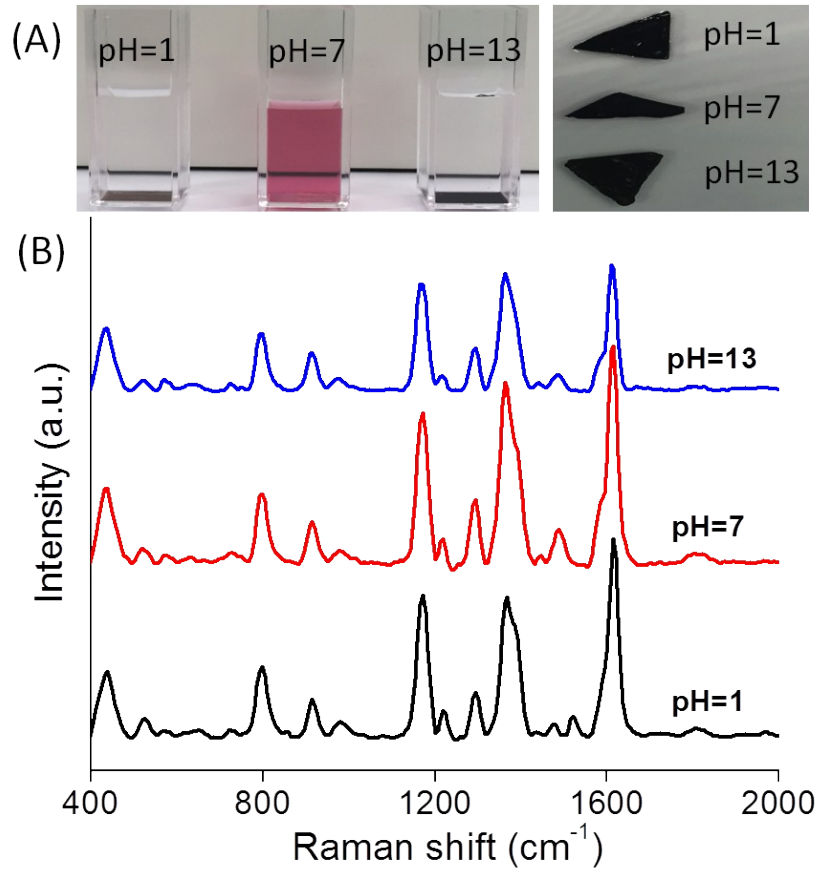

Figure S-6. A) AuNP suspension at different pH after settling for 6 h (left) and AuNP/BC nanocomposites taken out of MGITC solutions with different pH (right). B) Influence of solution pH on MGITC SERS spectra obtained with AuNP/BC as the SERS substrate.

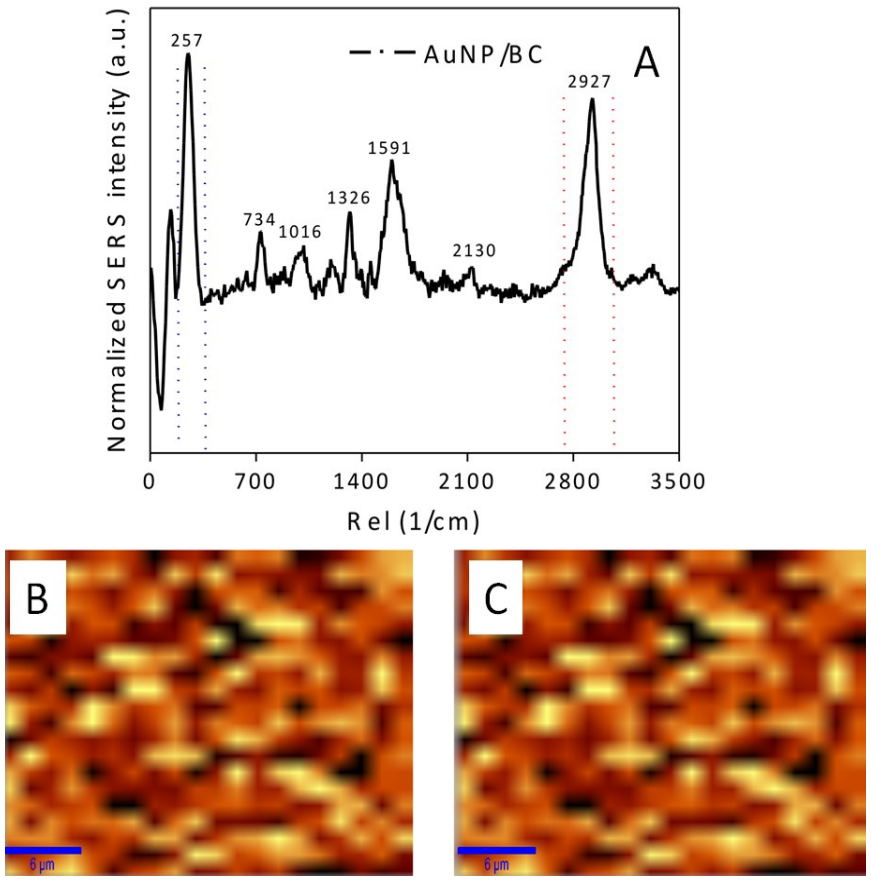

Figure S-7. A) Average Raman spectrum of AuNP/BC-1-10 (no added MGITC); Raman maps of B) nanocellulose and C) AuNPs. Each map covers a 32 µm × 16 µm area with 20 lines and 20 points per line. The integration time for each point was 0.5 s. A 10× objective and 0.26 mW laser intensity were used. The maps were obtained by tracking the intensity of the peak at 2927 cm^{-1} (B) or the peak at 257 cm^{-1} (C).

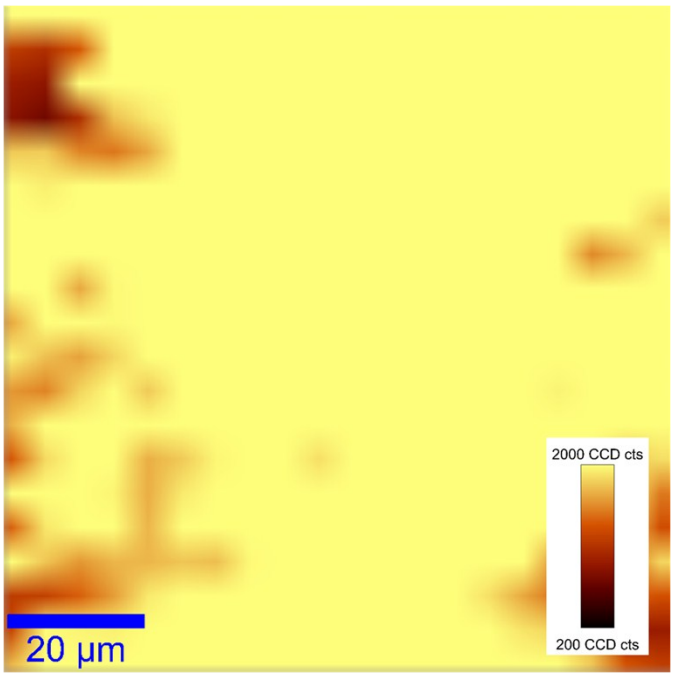

Figure S-8. Raman map of MGITC (100 nM) on AuNP/BC-1-10. The map was obtained by tracking the intensity of the peak at 1170 cm^{-1}.

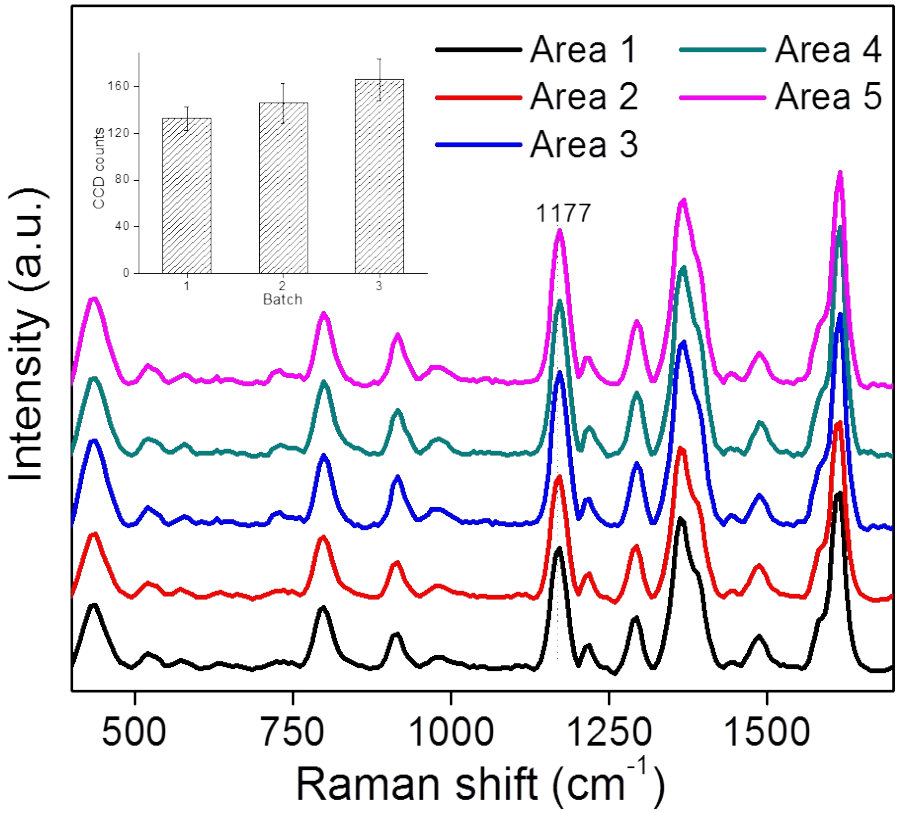

Figure S-9. Average SERS spectra of MGITC (1 μM) on five randomly selected areas on AuNP/BC-1-10. Inset is the intensity of Raman band at 1170 cm^{-1} of SERS spectra obtained by three batches of independently prepared AuNP/BC samples. There is no statistical difference between the average CCD counts for the three samples.

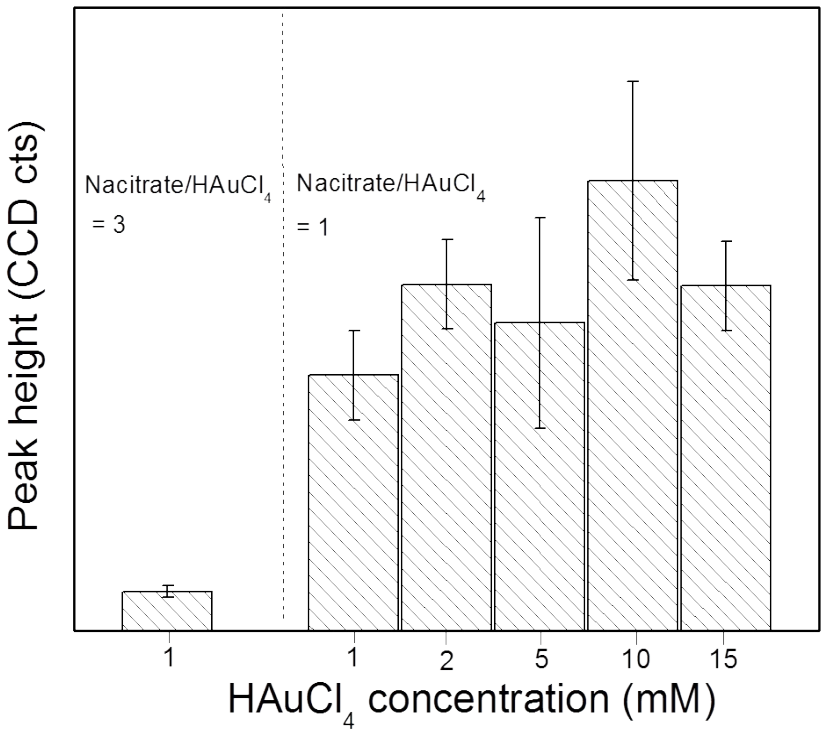

Fig. S-10. Raman signal intensity (denoted as the height of peak at 1170 cm^{-1}) of MGITC on AuNP/BC films prepared with different conditions of $HAuCl_4$ (each value is the average of three 100 μm × 100 μm image scans, each image scan is the average of 400 spectra, the error bars represent the standard deviation of replicate measurements).

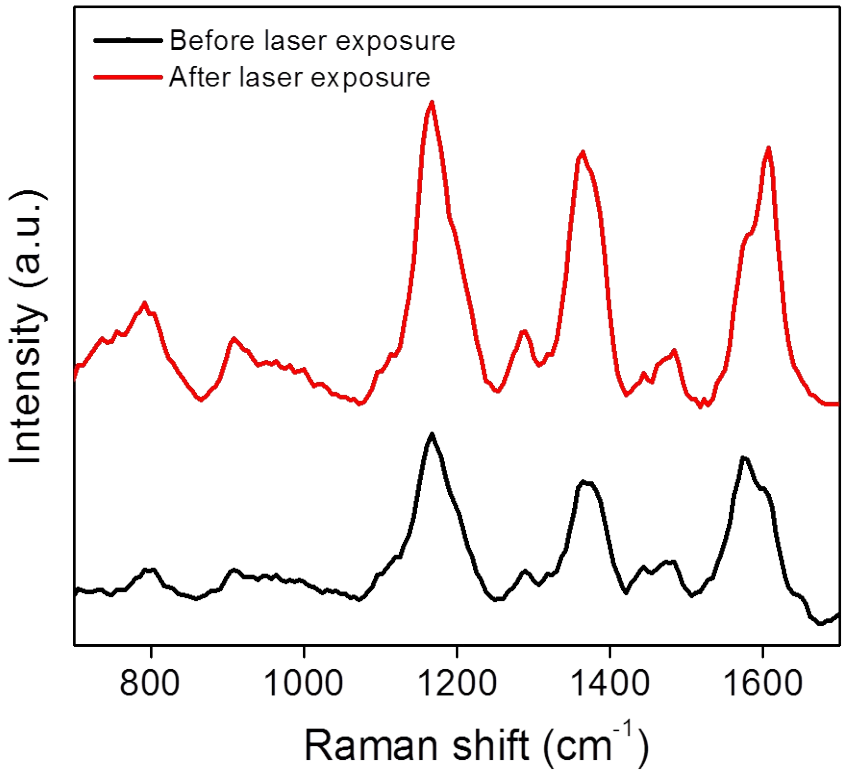

Figure S-11. Raman spectrum of MGITC on AuNP/BC-1-10 before and after laser exposure for 1 min.

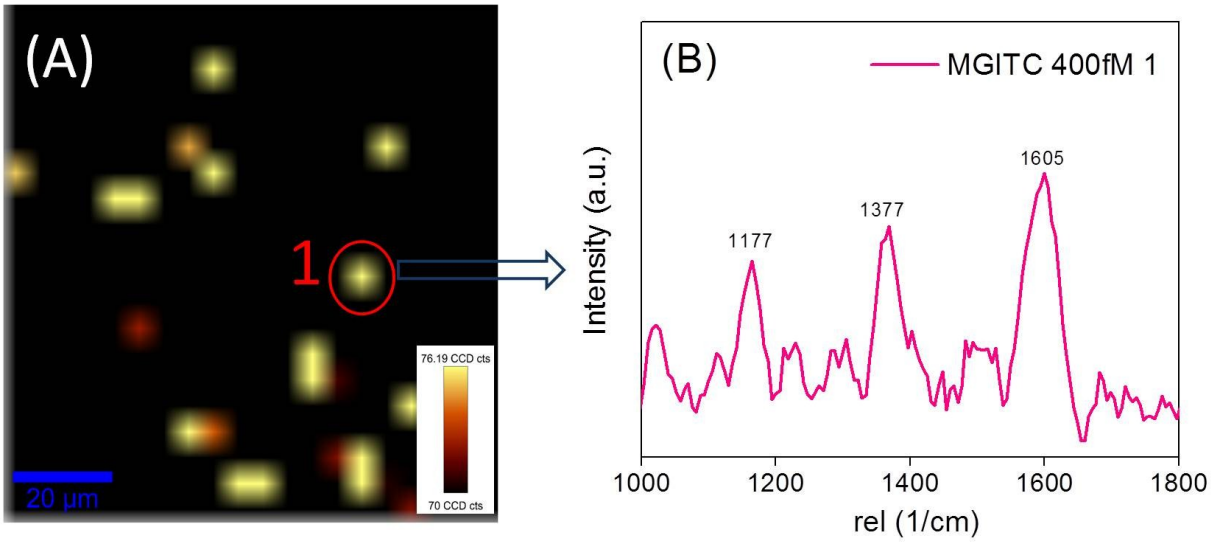

Figure S-12. A) Raman map of MGITC (400 fM) (The maps were obtained by tracking the intensity of peak at 1177 cm^{-1}) ; B) Raman spectrum at spot 1 labeled in the Raman map.

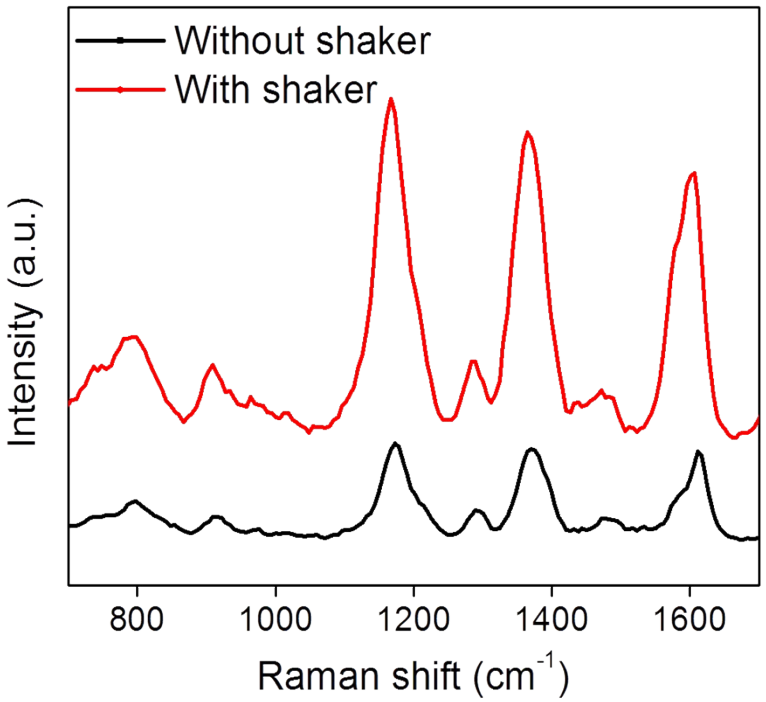

Figure S-13. SERS of MGITC (1 μM) on AuNP/BC-1-10 exposed to MGITC solution with or without a shaker.

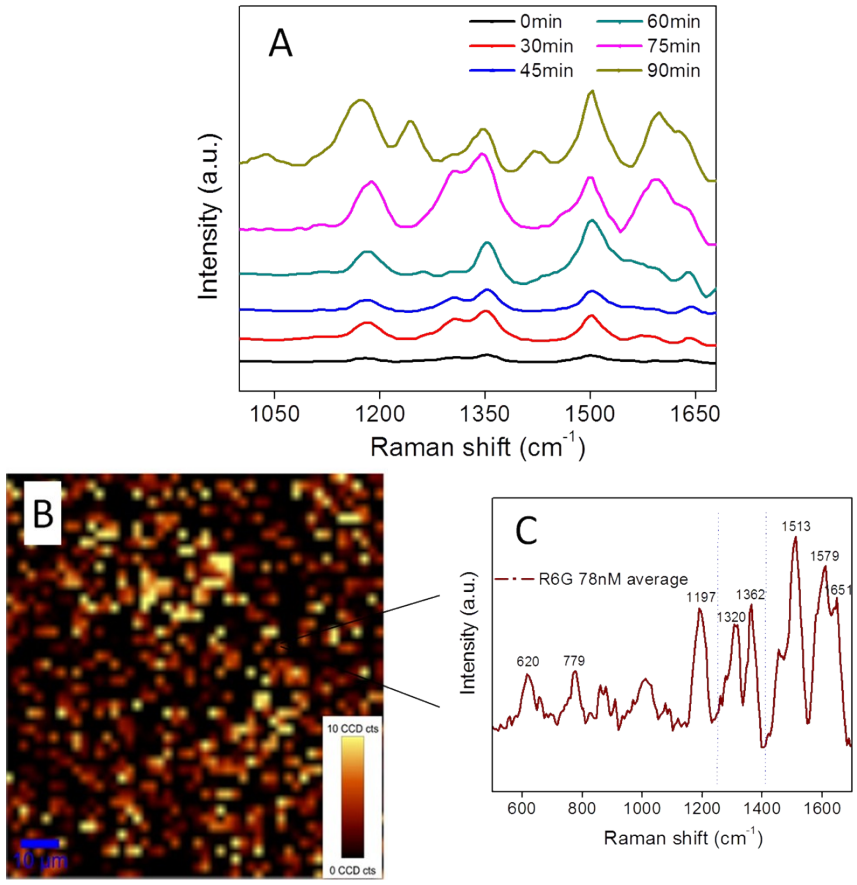

Figure S-14. A) SERS of R6G (7.8 µM) on AuNP/BC-1-10 as a function of drying time, B) image scan of R6G (78 nM) on AuNP/BC-1-10, and C) the average spectrum of R6G on AuNP/BC-1-10 in image scan. Image scan was acquired by tracking the area between 1250-1410 cm^{-1} (between the two dash lines).

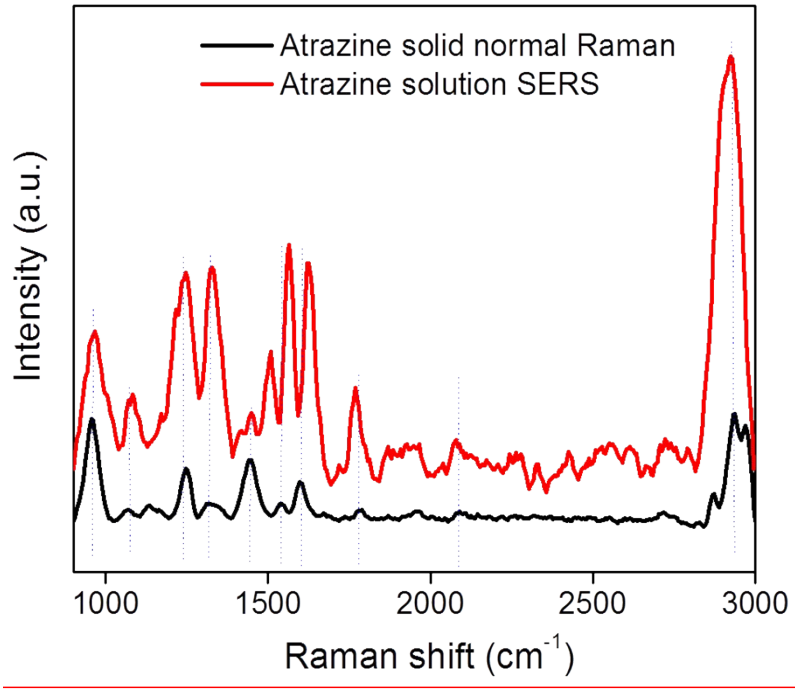

Figure S-15. SERS spectrum of atrazine (10 μM) on AuNP/BC-1-10 and normal Raman spectrum of atrazine solid.

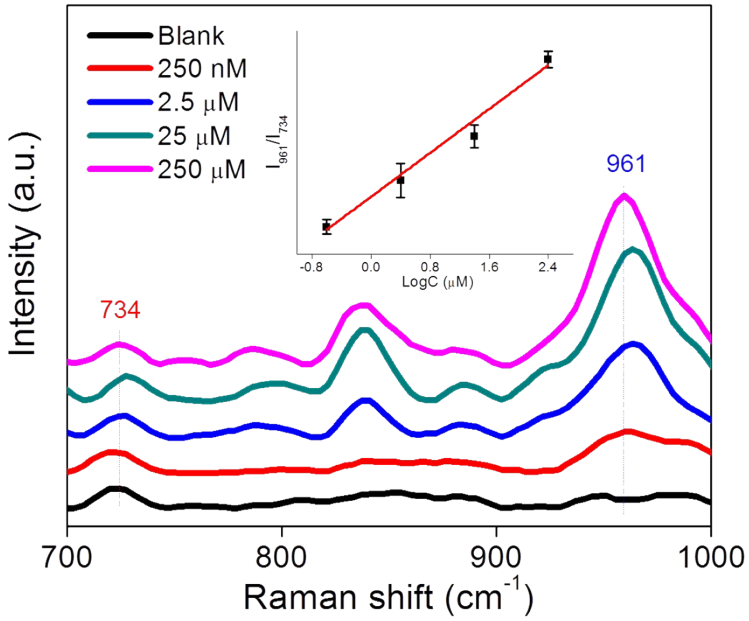

Figure S-16. Quantitative analysis of atrazine at a solution pH of 1.3. (Raman band at 734 cm^{-1} is from Na_3Cit coating and the Raman band at 961 cm^{-1} is from atrazine. Their intensity ratio I_{961}/I_{734} was used for the quantitative analysis of atrazine.)

References

1. Freus, G., Controlled nucleation for the regulation of the particle size in monodisperse gold solutions. *Nature (Phys Sci)* **1973,** *241*, 20-22.

2. Brown, K. R.; Walter, D. G.; Natan, M. J., Seeding of colloidal Au nanoparticle solutions. 2. Improved control of particle size and shape. *Chem. Mater.* **2000,** *12*, (2), 306-313.