Supporting Information

Fe_3O_4/Au Nanoparticles/Lignin Modified Microspheres as Effectual Surface Enhanced Raman Scattering (SERS) Substrate for Highly Selective and Sensitive Detection of 2,4,6-Trinitrotoluene (TNT)

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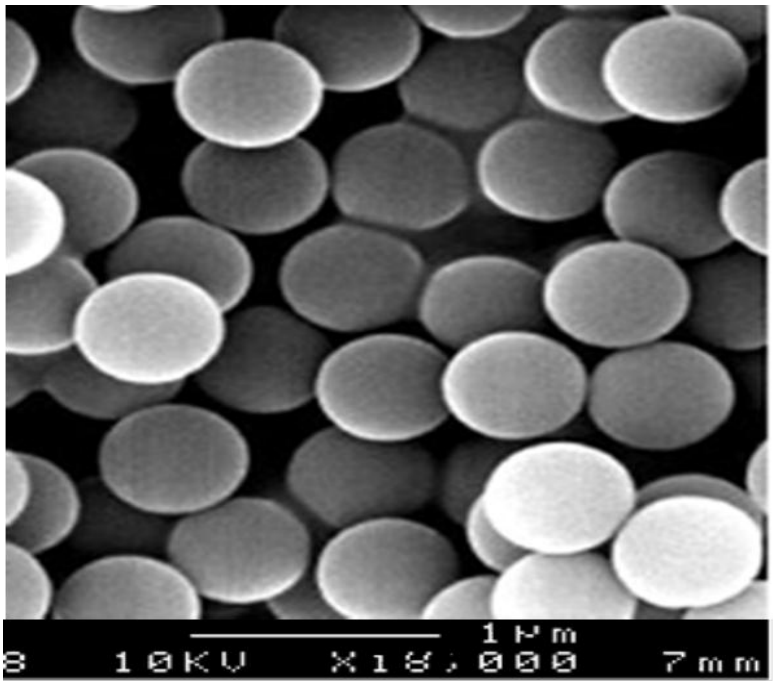

Fig. S1: FE-SEM image of PSA microspheres.

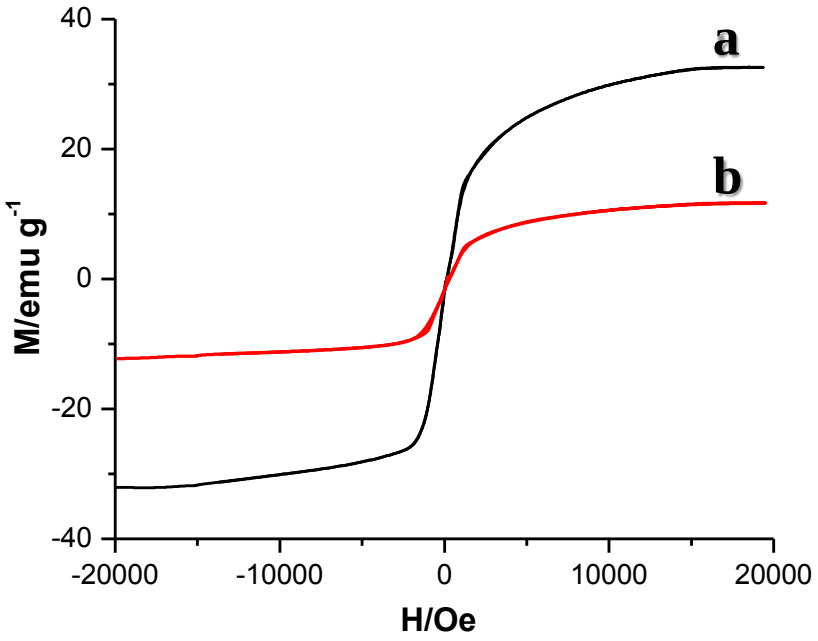

Fig. S2: Room-temperature magnetic hysteresis curves for (a) PSA/SiO_2/Fe_3O_4; PSA/SiO_2/Fe_3O_4/AuNPs (MMS) microspheres.

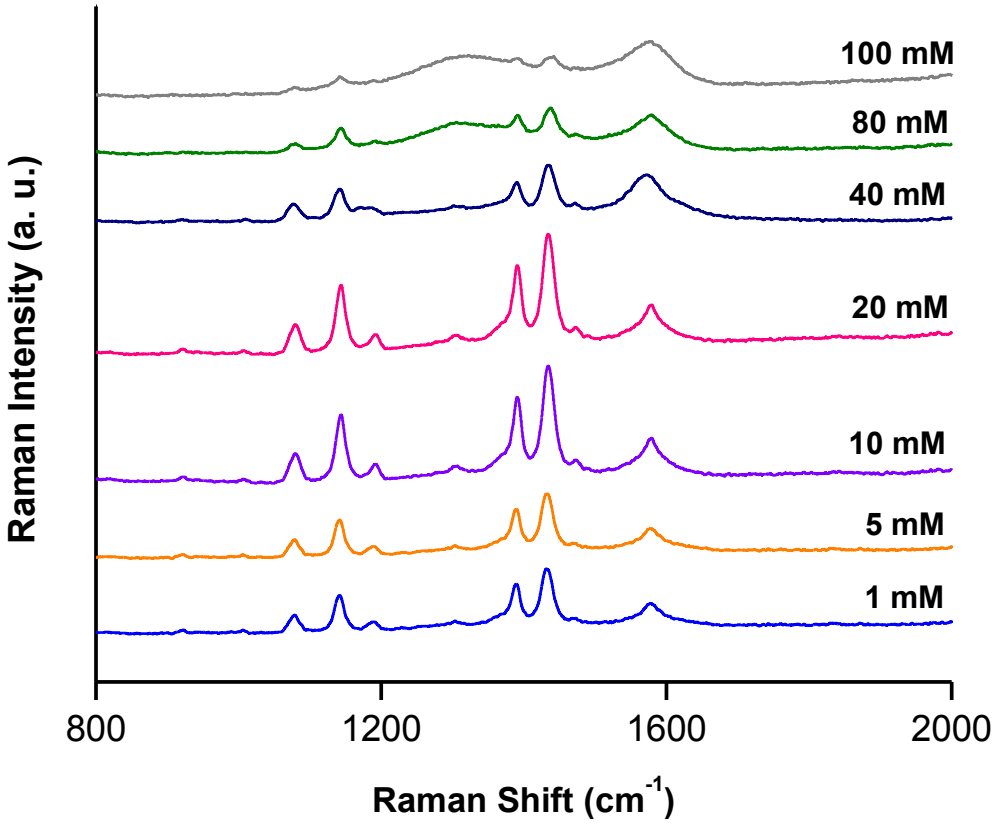

Fig. S3: Raman Intensity of 4-ABT modified L-MMS substrate at increasing initial concentration of lignin (1-100 mM).

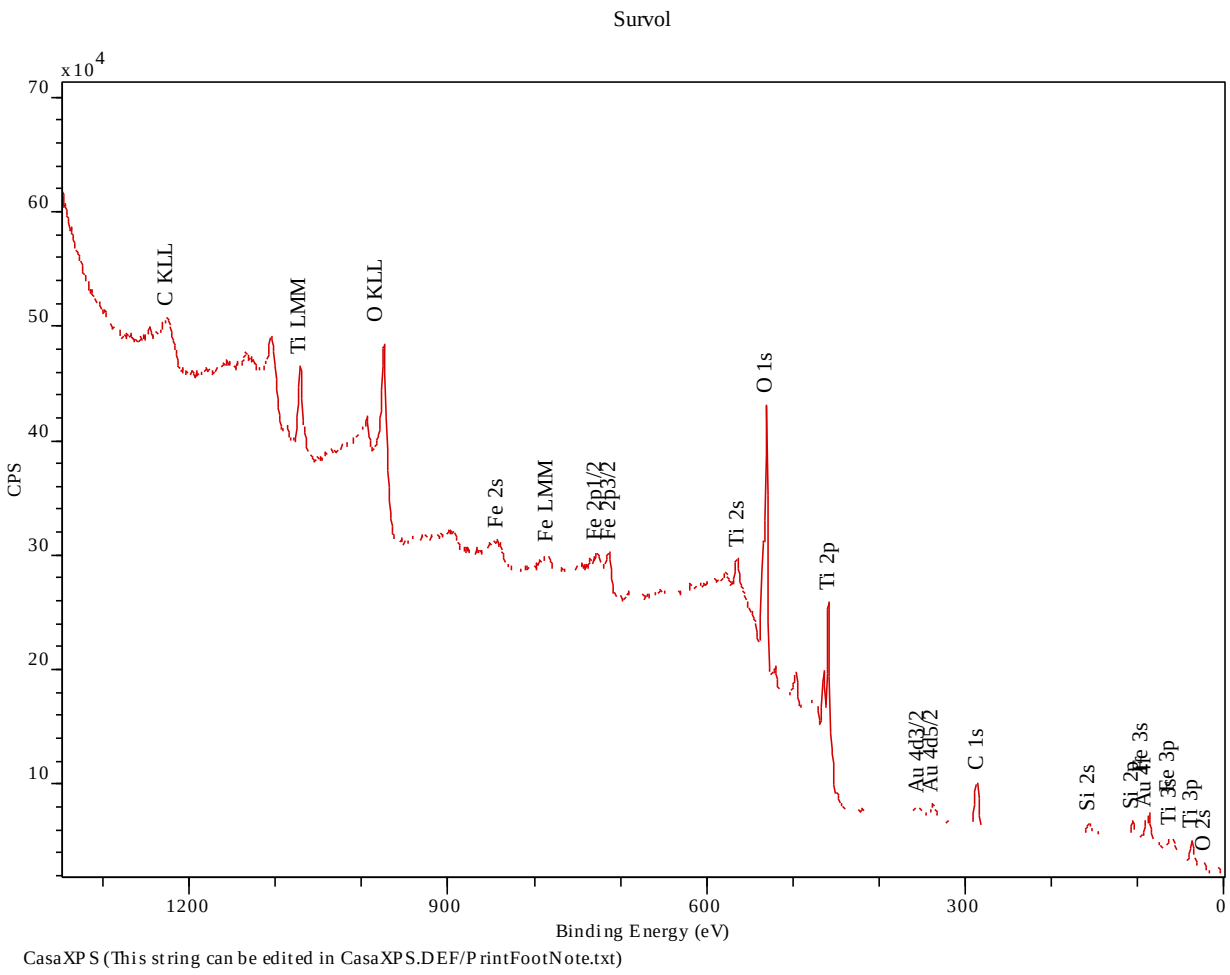

Fig. S4: XPS image of L-MMC.

Samples	Au 4f	C 1s	Fe 2p	O 1s
L-MMC	1.1	30.9	5.4	62.6
MMC	1.9	24.2	9.6	64.3

Table S1: Atomic concentration (%) of L-MMC and MMC microspheres from xps experiment.

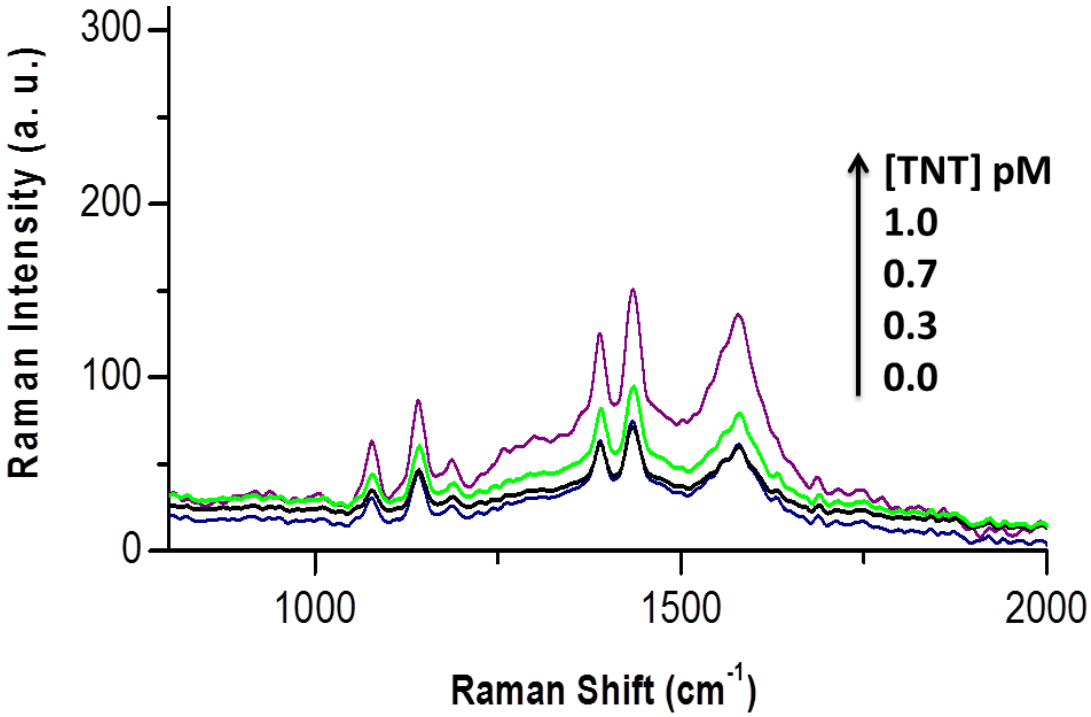

Fig. S5 Evaluation of Raman spectra of 4-ABT modified L-MMS with the increase of TNT concentrations from 0 pM to 1 pM. The green spectrum represents 0.7 pM. Each spectrum represents an average of three repeated measurements. The error range of each spectrum was less than 5%.

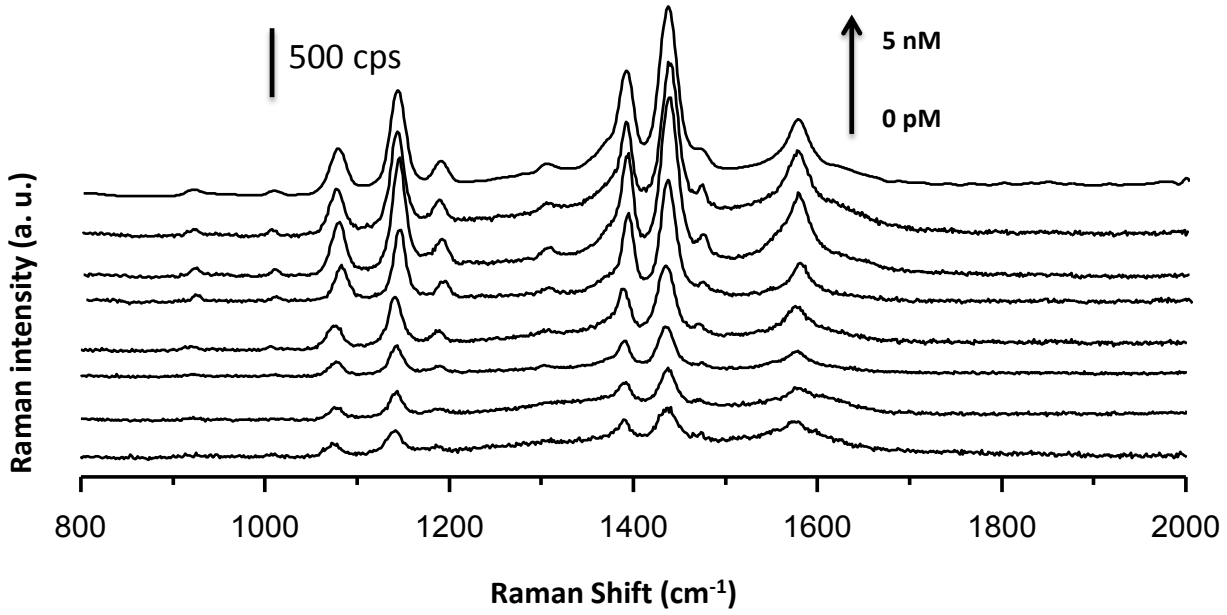

Fig. S6a: Raman intensity of MMS substrate with increasing concentration of TNT

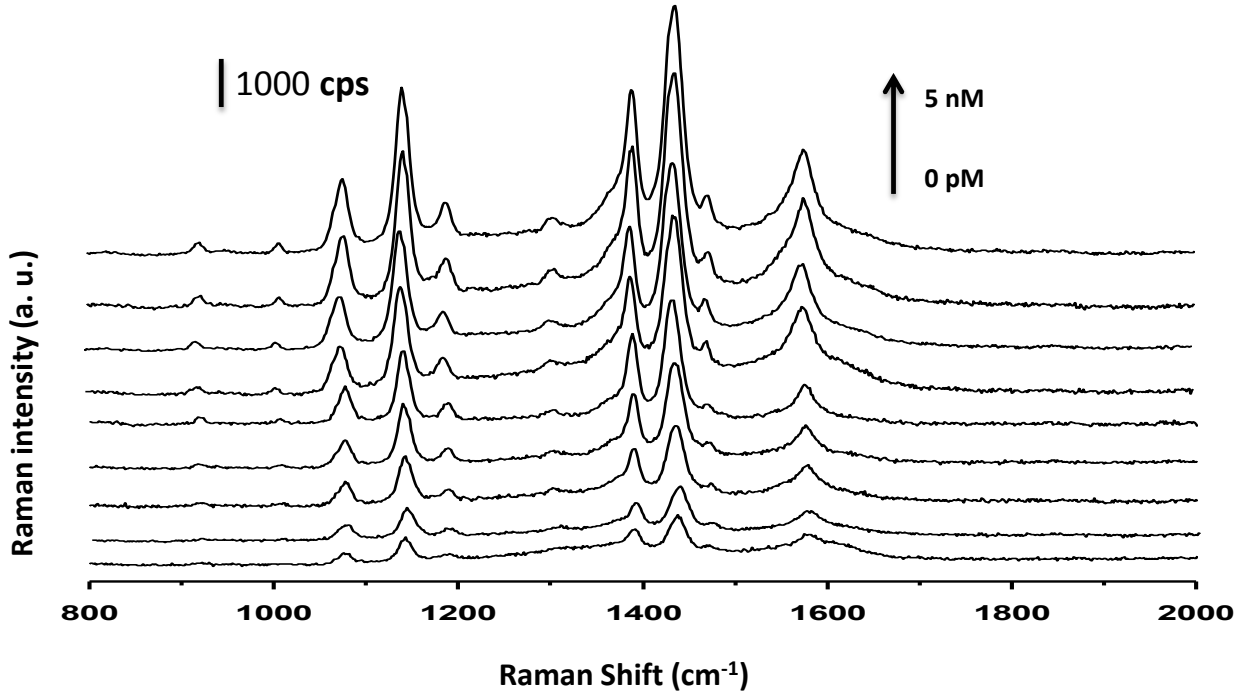

Fig. S6b: Raman intensity of L-MMS substrate with increasing concentration of TNT.

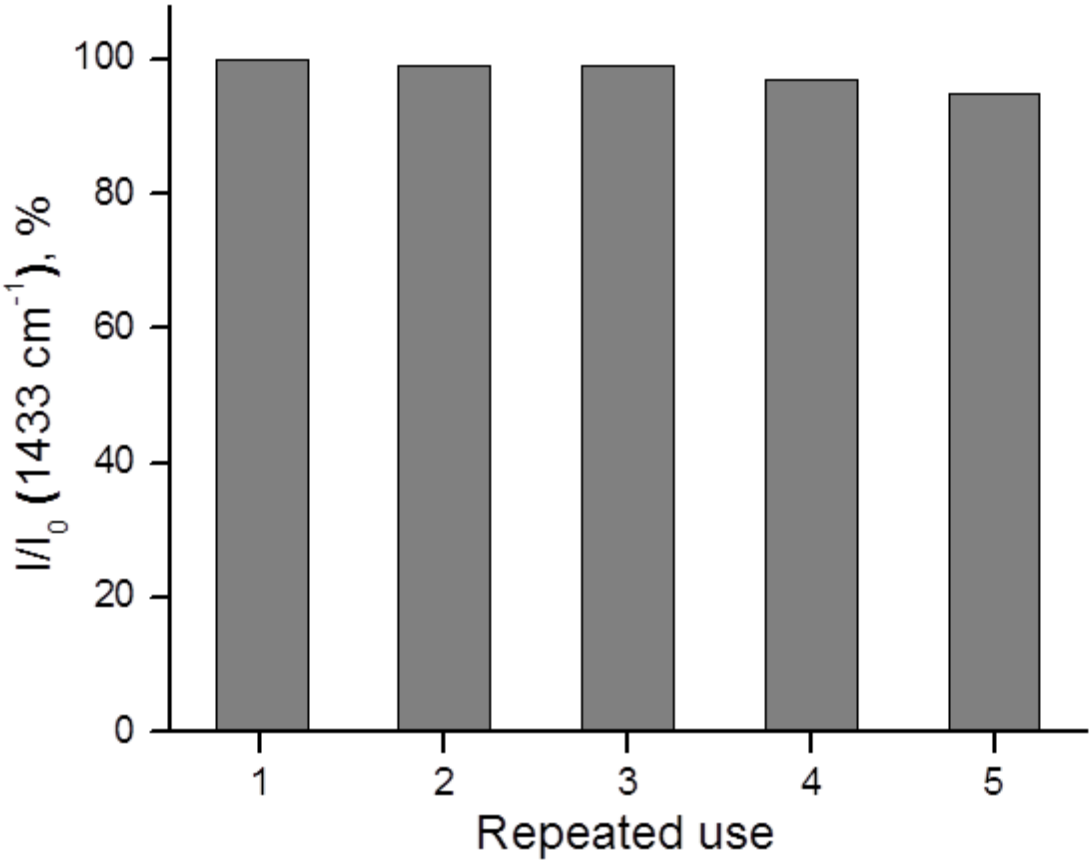

Fig. S7: Effect of repeated use on the % recovery of L-MMS substrate. Experiment was repeated 5 times at the same condition for 0.1 µM TNT. I/I_o is the relative SERS intensity at 1433 cm^{-1} after each repeated cycle.

Enhancement Factor (EF) calculation:

SERS enhancement factor (EF) was calculated by comparing the intensity of the appropriate 4-amino benzenethiol (4-ABT) peak (~1433 cm^{-1}) measured in the SERS experiments from 4-ABT modified PSA/SiO_2/Fe_3O_4/AuNPs (MMS or L-MMS) to the corresponding peak measured from 4-ABT on unmodified substrate. The SERS enhancement factor (EF) is given by:

$$EF = I_{SERS}\, N_{Vol} / I_{RS}\, N_{Surf}$$

Where: $N_{Vol} = C_{RS}V$ is the average number of molecules in the scattering volume (V) at concentration C_{RS} for the Raman (non SERS) measurement, and N_{Surf} is the average number of adsorbed molecules in the scattering volume for the SERS experiments. For the normal Raman the probed volume was assumed to be a cylinder with a diameter of 25 μm (minimum diameter of focused laser) and a height of 1μm (approximate focus depth of laser). For all calculations, the surface of the microsphere was assumed to be saturated with 4-ABT molecules. The molecules occupy 20 $Å^2$ and the probed surface area was a circle with a diameter of 25 μm. The EF was calculated three (3) times and the results were similar for each SERS substrate.

References:

[1] a) R.P. Van Duyne, J.C. Hulteen, D.A. Treichel, *J. Chem. Phys.* **1993**, 99, 2101-2115; b) B. Nikoobakht, J. Wang, M.A. ElSayed, *Chem. Phys. Lett.* **2002**, 366, 17-23.

[2] a) P. Hildebrandt, M. Stockburger, *J. Phys. Chem.* **1984**, 88, 5935-5944; b) K. Kneipp, E. Roth, C. Engert, W. Kiefer, *Chem. Phys. Lett.* **1993**, 207, 450-454.