Supporting Information

Fe₃O₄/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$_3$O$_4$; PSA/SiO$_2$/Fe$_3$O$_4$/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-MM C.

**Table S1:** Atomic concentration (%) of L-MM C 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\(_3\)O\(_4\)/AuNPs (MMS or L-MMS) to the corresponding peak measured from 4-ABT on unmodified substrate. The SERS enhancement factor (EF) is given by:

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EF = \frac{I_{\text{SERS}}}{I_{\text{RS}}} \frac{N_{\text{Vol}}}{N_{\text{Surf}}}
\]

Where: \(N_{\text{Vol}} = C_{\text{RS}}V\) is the average number of molecules in the scattering volume (V) at concentration \(C_{\text{RS}}\) for the Raman (non SERS) measurement, and \(N_{\text{Surf}}\) 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:**
