Supporting Information

Modification of Ag nanoparticles with mixed thiols for improved SERS detection of poorly adsorbing target molecules: detection of MDMA

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S.1 – Other Thiols Studied

Several other thiol mixtures were tested for their ability to detect MDMA, including mixtures of the alkanethiols, propanethiol (P3T), pentanethiol (P5T) or decanethiol (DT), and mercaptopropanesulfonic acid (MPA). Mixtures of benzyl mercaptan (BZM) and P5T were also studied under alkaline conditions. It was found that MPS-P3T, MPS-P5T and MPS-DT mixtures were capable of adsorbing 7.7×10^{-4} M MDMA. The spectra in Figure S1 show the best results from each series of mixed feedstocks after subtraction of the blank monolayer.

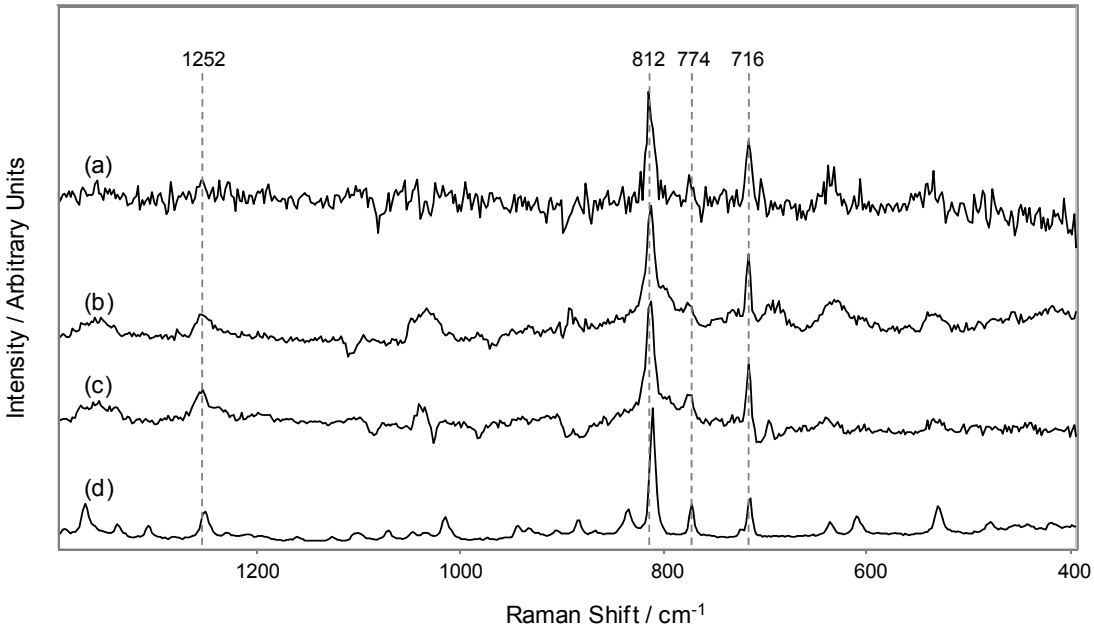

Figure S1 SERS spectra of 7.7×10^{-4} M MDMA adsorbed to (a) MPS-DT SAM made from 75% MPS/25% DT feedstock, (b) MPS-P5T SAM made from 50% MPS/50% P5T feedstock and (c) MPS-P3T SAM made from 50% MPS/50% P3T feedstock after subtraction of the appropriate blank. (d) Raman spectrum of solid MDMA.HCl is shown for reference. Spectra are scaled and vertically offset for clarity.

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While these monolayers were capable of MDMA detection, they were outperformed by MPS-BZM layers. Furthermore, P5T-BZM monolayers did not effectively adsorb MDMA at any of the concentrations studied, and no signal from the analyte could be observed.

S.2 MPS-BZM Monolayer Efficacy Plot

The range of mixed SAMs varied tremendously in their ability to detect MDMA. To study this further, the spectra of SAMs spiked with MDMA were recorded, the appropriate blank signals subtracted, and the heights of two peaks at 812 cm^{-1} and 716 cm^{-1} were measured. The heights for the full range of monolayers at MDMA concentrations of $7.7x10^{-4}$ M and $7.7x10^{-5}$ M are plotted in Figure S2 (a) and (b), respectively.

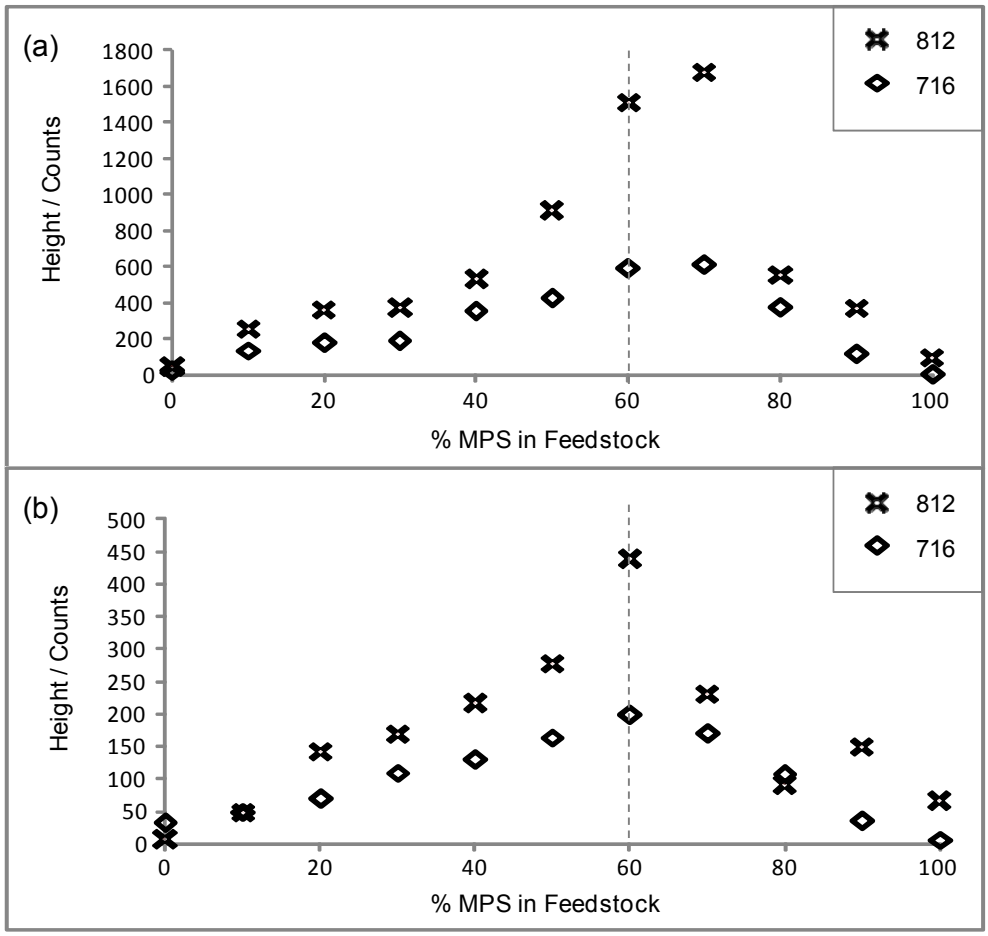

Figure S2 Representative plots of the heights of 812 cm^{-1} peak (✖) and 716 cm^{-1} peak (◆) after subtraction of the blank monolayer at (a) $7.7x10^{-4}$ M and (b) $7.7x10^{-5}$ M MDMA. Peak heights at 60% have been highlighted for clarity.

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S.3 UV-Vis Spectra for MPS-BZM Mixed Monolayers

Figure S3 shows the UV-vis absorption spectra of HRSC modified with various mixed monolayers of MPS and BZM. To obtain reasonable spectra in 1 cm pathlength cells, it was necessary to dilute HRSC by 5:1 (H_2O : HRSC); otherwise the absorbance was too high (3.5 - 4) to measure accurately. The dilution would increase the inter-particle distance and therefore slow aggregation, so samples were modified before dilution to produce more meaningful results. 40 µL modifying feedstock was added to 400 µL HRSC (*i.e.* in the same proportions as for the Raman experiments) in a disposable plastic cuvette (10 mm pathlength) and stirred vigorously for 10 seconds. 2 mL DDI H_2O was added to this mixture and the spectrum recorded using an Agilent 8453 single beam diode array spectrophotometer. Unmodified HRSC diluted to the same extent (black trace), and the unmodified HRSC aggregated with 160 µL 1 M NaCl (black dashed trace) are shown for reference.

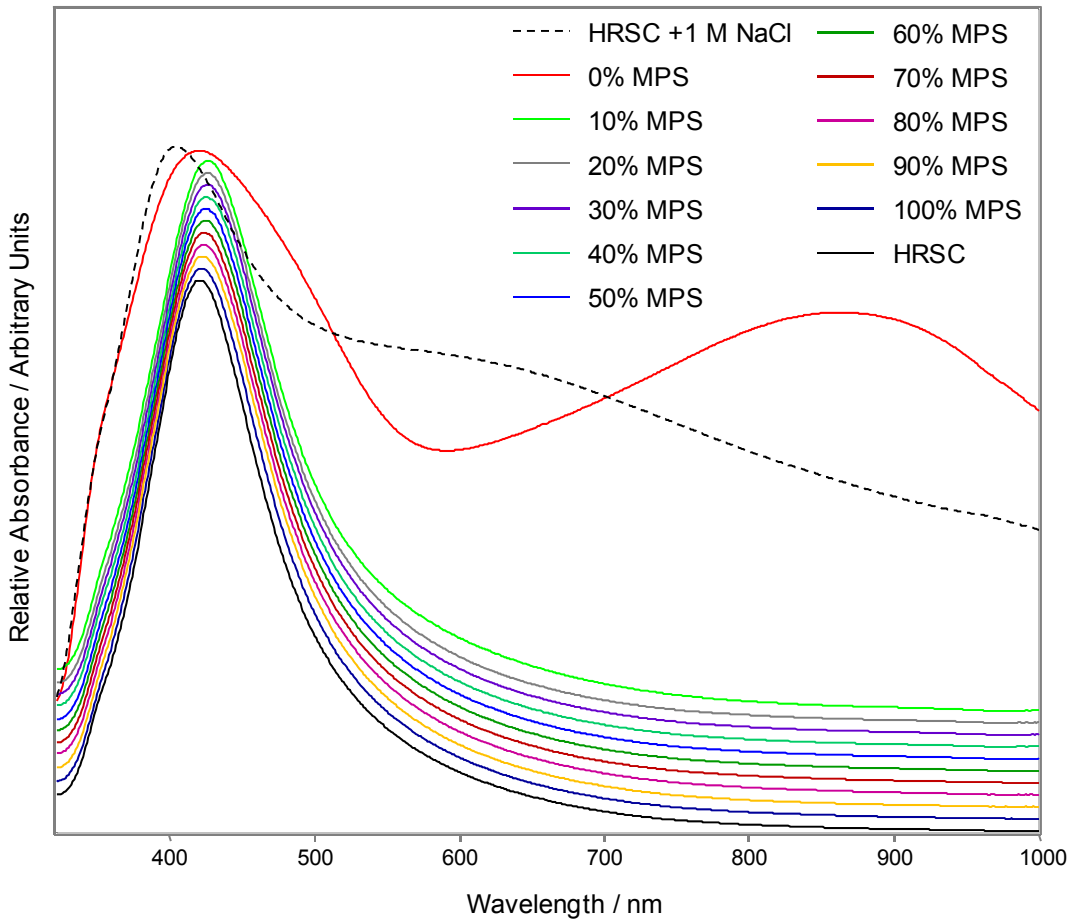

Figure S3 UV/vis absorption spectra of HRSC modified with various mixed SAMs of MPS and BZM. Spectra have been normalized to the highest band and vertically offset slightly for clarity.

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As shown in Figure S3, the colloids modified with 10-100% MPS showed very little or no aggregation, while the colloid modified with 0% MPS (100% BZM0 had completely aggregated within a few seconds of modification.