***Supporting Information*:** Title

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Silanization of glass bubbles: 0.3g of S60/10000 3M Glass bubbles (average diameter 30 μm, density 0.6 g/mL) were added to 10N H_2SO_4 overnight to activate the glass surface.[1] Silanization of the activated glass bubbles was achieved via exposure to a 10% solution (v/v) of 3-aminopropyltriethoxysilane in methanol overnight with constant rocking. The glass bubbles were subsequently washed 6 times with methanol and re-suspended in 3 mL HPLC grade H_2O for future use.[2]

Preparing and shelling Au nanoparticles (AuNPs): AuNPs were prepared by the Frens method.[3] 200mL of HPLC grade H_2O was added to a beaker and warmed on a hot plate. Once the water was warmed to approximately 30˚C, 20 mg of $HAuCl_4$ was added to the solution and brought to a rolling boil. 1200 μL of 1% (wt/vol) $Na_3C_6H_5O_7$ was then added all at once. The solution

boiled for one hour with a watch glass placed over the beaker. The solution was then removed from the heat and allowed to cool to room temperature prior to storage. This method of synthesis produced AuNPs with an average diameter of approximately 50 nm as determined by SEM. The concentration of the AuNP solution was 6.0 x 10^{10} AuNPs/mL by a method similar to that of Haiss et. al.[4]

Modification of glass bubbles with gold nanoparticles: Immediately following sufficient agitation of the silane-treated glass bubble solution, 200 μL was added to a 1.75 mL Eppendorf tube. The glass bubbles were allowed to float to the surface and the supernatant was removed with a 1 mL syringe and 26-gauge needle. The glass bubbles were rinsed at least 5 times with 200 μL of 50% (v/v) MeOH solution in water to remove excess APTES: For each wash, 200 μL of the MeOH solution was added and the sample was agitated at room temperature for ca. 2 minutes. 1 mL of HPLC H_2O was then added to the glass bubble MeOH solution to facilitate floatation of the glass bubbles. The supernatant was carefully removed and the rinse procedure was performed at least 4 more times with the supernatant being completely removed on the final rinse. Next, 200 μL of Au nanoparticles (AuNPs) were added to these rinsed glass bubbles. The mixture was agitated at room temperature until the solution became almost clear. The glass bubbles were allowed to float to the top of the solution and the supernatant was removed. AuNPs were added in 200 μL volumes and agitated until the solution remained purple. The resulting Au coated glass bubbles were re-suspended in 500 μL of HPLC grade H_2O.

Concentration of Au coated glass bubbles: 10 μL of the Au-coated glass bubble solution was added to a microscope slide and allowed to dry. An Olympus BX51 microscope was used to determine the counting area of the bubble solution and the bubbles in this area were enumerated.

Based on the total area of the solution and the numbers of bubbles counted, we approximated the concentration of Au-coated glass bubbles to be 1 x 10^5 bubbles/mL.

Instrumentation: All spectroscopic data was collected using a Snowy Range Instruments IM 52 808 nm laser Raman system with rastering capability. The rastering addition maintains small laser spot size while averaging over an elliptical area of ca. 2 mm x 0.5 mm.

Surface-enhanced Raman spectroscopy (SERs) of AuNPs added to aqueous CN^- solutions: 30 μL of AuNPs (1.8 x 10^9 nanoparticles) were added to an equal volume of sodium cyanide solution buffered at pH = 9 (4:1 (v/v) 0.1M $NaHCO_3$:0.1M Na_2CO_3 buffer). Cyanide solutions of varying concentrations (200 parts per million (ppm) to 2 parts per billion (ppb)) were titrated while maintaining constant volumes from sample to sample. Upon addition of AuNPs to the CN^- solutions, each sample was incubated for 5 minutes with gentle agitation at room temperature. The entire volume was pipetted onto a steel substrate for interrogation with the laser. Each spectrum was acquired for 0.5 sec and the intensity was plotted against the cyanide concentration. Each data point was replicated 5 times for the same integration time and error bars on graph are +/- 1 standard deviation of all 5 replicates.

SERs of Au-coated glass bubbles added to aqueous CN^- solutions: 10 μL of Au-coated glass bubble solution (1.5 x 10^6 Au-coated glass bubbles) was added to 40 μL of sodium cyanide solution buffered at pH = 9 (4:1 0.1M $NaHCO_3$:0.1M Na_2CO_3 buffer). Cyanide solutions of varying concentrations (200 parts per million (ppm) to 2 parts per billion (ppb)) were titrated while maintaining constant volumes from sample to sample. Samples were incubated for 5 minutes with gentle agitation at room temperature. The entire volume was pipetted onto a steel substrate for interrogation with the laser. The Au-coated glass bubbles were allowed to float to

the top of each sample prior to analysis and they formed a small circular island in the middle of each sample. Once this was observed, each spectrum was acquired for 0.1 sec and the intensity was plotted against the cyanide concentration. Each data point was replicated 5 times for the same integration time and error bars on graph are +/- 1 standard deviation of all 5 replicates.

SERs of varying amounts of Au-coated glass bubbles added to CN^- solutions of constant concentration: In each trial, the CN^- concentration was held at 1 ppm. The amounts of Au-coated glass bubbles were varied, but the amount of solution containing the Au-coated glass bubbles was held constant for each sample. Dilutions of the Au-coated glass bubbles were made as follows from 500 μL of the Au-coated glass bubble stock solution: 80 μL stock solution was added to 20 μL H_2O, 60 μL stock was added to 40 μL H_2O, 40 μL stock was added to 60 μL H_2O, and 20 μL stock was added to 80 μL H_2O. 10 μL of each dilution was added to 30 μL of 1ppm CN^- solution. 10uL of the undiluted stock solution was also added to 30 μL of 1 ppm CN^- solution, and 10 μL water was added to 30 μL of 1 ppm CN as a negative control. Samples were mixed with gentle agitation for 3 minutes at room temperature. The entire volume was pipetted onto a steel substrate for interrogation with the laser. The Au-coated glass bubbles were allowed to float to the top of each sample prior to analysis and they formed a small circular island in the middle of each sample. Each spectrum was acquired for 0.5 sec and the intensity was plotted against the Au-coated glass bubble concentration. Each data point was replicated 5 times for the same integration time and error bars on graph are +/- 1 standard deviation of all 5 replicates.

References

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