

ESI

Experimental

DNA oligonucleotides were purchased from ATD Bio, Southampton and malachite green isothiocyanate was purchased from Invitrogen, Paisley.

Thiol modified DNA (10 nmoles): 5' SH (HEG)₃ TCT CAA CTC GTA 3' and 5' SH (HEG)₃ CGC ATT CAG GAT 3' was added to 13 nm citrate-reduced gold nanoparticles (1 mL, 4.5 nM) and 35 nm silver nanoparticles (1 mL, 0.4 nM), respectively, and salt-aged as previously reported.^[1] Nanoparticle conjugate concentrations were evaluated using extinction spectroscopy ($\epsilon = 2.87 \times 10^{10} \text{ M}^{-1} \text{ cm}^{-1}$ at 400 nm for silver^[2] and $\epsilon = 2.7 \times 10^8 \text{ M}^{-1} \text{ cm}^{-1}$ at 520 nm for gold^[3]).

Malachite green isothiocyanate, MG ITC, (500 μL , 1 μM) was added to the oligonucleotide gold nanoparticle conjugate (500 μL , 6.7 nM) and incubated for 16 hours in the dark, followed by centrifugation and resuspension in 0.3 M PBS. The nanoparticle assembly was constructed by hybridisation of the target sequence: 5' ATC CTG AAT GCG TAC GAG TTG AGA 3' (50 nM) with the MG ITC labelled oligonucleotide functionalised gold conjugate (0.5 nM) and the oligonucleotide silver conjugate (50 pM).

SERRS spectra were recorded from a cuvette 5 minutes after the addition of the target sequence using a Renishaw System 2000 spectrometer equipped with a Vantacon macrosampler. The laser excitation source was a 632.8 nm He Ne laser. UV-visible spectra were recorded using a Varian Cary Bio 300 spectrometer.

[1] McKenzie, F.; Faulds, K.; Graham, D. *Small* **2007**, 3, 1866-1168.

[2] Yguerabide, J.; Yguerabide, E. E. *Anal. Biochem.* **1998**, 262, 137-156.

[3] Jin, R. C.; Wu, G. S.; Li, Z.; Mirkin, C. A.; Schatz, G. C. *J. Am. Chem. Soc.* **2003**, 25, (6), 1643-1654.