Supporting Information

Synthesis and NIR Optical Properties of Hollow Gold Nanospheres with LSPR Greater than One Micrometer

*Hai-nan Xie, Iain A. Larmour, Yi-Chieh Chen, Alastair W. Wark, Vasiliki Tileli, David W. McComb, Karen Faulds, Duncan Graham**

Further discussion about the synthesis of hollow gold nanospheres

The reproducibility of the synthesis is determined by several factors. First, the glassware should be clean without any organic residues. This can be done by rinsing the glassware with aqua regia following by piranha solution. (Caution: the aqua regia should be completely removed and rinsed with water several times before the addition of the piranha solution.) Second, the quality of the hollow gold nanospheres is decided by the quality of the cobalt nanoparticles. Sometimes, after the addition of 1 mL of 0.1 M $NaBH_4$, a grey coloration was obtained which meant highly poly-dispersed Co nanoparticles. This can be solved by further removing the dissolved oxygen in the main solution and increasing the mixing speed. $NaBH_4$ was dissolved in oxygen free water which also enhances the synthesis quality. Bubbling Argon into the solution is a good way of mixing when a magnetic stirrer needs to be avoided to solve both mixing and dissolved oxygen problems. Finally, although reducing the amount of sodium citrate can increase the size of the Co nanoparticles which would produce more red-shifted hollow gold nanospheres, the Co nanoparticles would aggregate if insufficient citrate were present. Therefore, a balance should be found here. Occasionally, when the flask was replaced, different results were obtained. This is probably due to the presence of scratches inside the original or replacement flask which might change the reaction dynamics and therefore the result. However, the exact mechanism is still unknown. To obtain constant results, the same flask is recommended but the different results between flasks can be compensated for by tuning the amount of sodium citrate and the concentration of the gold ions. In addition, both Milli-Q water and double distilled water were used for the synthesis and no differences were found. The detailed parameters used in this work can be found below.

	HGN-650	HGN-775	HGN-1080	HGN-1320
Added volumes of 0.1 M trisodium citrate dihydrate (μL)	650	450	400	400
Concentrations of chloroauric acid trihydrate (μM)	130	25	15	10
Added volumes of 0.6 mM sodium citrate solution after centrifugation (mL)	15	7.5	5	2

To be noted, as mentioned previously, different flasks might lead to different results. Therefore, the given parameters are subject to change in individual cases.

Details of the derivation of the absorption efficiency

Volume of the focus beam $V = 3.21 \times \lambda^3 \times \left(\frac{f}{D}\right)^4$ (1)

The focal length of field penetration of the laser into the sample $h = n \times \frac{\lambda}{N.A.^2}$ (2)

$N.A. = \frac{1}{2 \times f_{ND}}$ (3)

$f_{ND} = \frac{f}{D}$ (4)

Cross sectional area of the laser beam (CSA)= $\frac{V}{h}$ (5)

Power density in the focus area= $\frac{laser\ power}{CSA}$ (6)

CSA of a nanoparticle = $\pi \times r^2$ (7)

Work= CSA of nanoparticle × Power density × Time (8)

Number of nanoparticles= $N_A \times C \times V$ (9)

Total theoretical work= Work× Number of nanoparticles (10)

Actual work=$C_{water} \times m_{water} \times \Delta T$ (11)

Efficiency η=$\frac{Actual\ work}{Total\ theorectical\ work}$ (12)

η= $\frac{C_{water} \times m_{water} \times \Delta T \times D^2}{4 \times N_A \times C \times \pi r^2 \times n \times P \times \lambda \times f^2 t}$ (13)

λ is the excitation wavelength; f is the focal length; D is the lens diameter; n is the refractive index of the surrounding media; N_A is Avogadro constant; N.A. is the numerical aperture; r is the average radius of the nanoparticles; C is the concentration of the nanoparticles and t is the illumination time. Equations 1-4 are from Ref. 1.

	Zeta potentials (mv)	*Outer Diameters (nm)*	*Shell thickness (nm)*	*Concentrations (particles/mL)*
Ag nanoparticles	*-40.8±3.20*	*46±2*	*NA*	*2.02×10^{11}*
Au nanoparticles	*-40.2±3.15*	*45±5*	*NA*	*1.92×10^{11}*
HGN 650	*-42.9±3.36*	*53±8*	*8.3 ± 0.6*	*1.89×10^{11}*
HGN 775	*-42.0±3.48*	*66±11*	*6.5 ± 1.3*	*$\sim1.99\times10^{11}$*
HGN 1080	*-39.1±3.27*	*67±14*	*NA*	*$\sim2.28\times10^{11}$*
HGN 1320	*-41.1±2.97*	*87±19*	*NA*	*NA*

Table S1. Further physical details about the nanoparticles. Size distributions were obtained by counting at least 200 individual nanoparticles from SEM images through Image J. A typical SEM and TEM image of HGN-775 which was used for counting is shown in figure S4. Due to the limitation of the laser excitation wavelength (640 nm) inside the nanosight instrument, the concentration results for nanoparticles with a LSPR larger than 800 nm are not very accurate therefore, these are the approximate values.

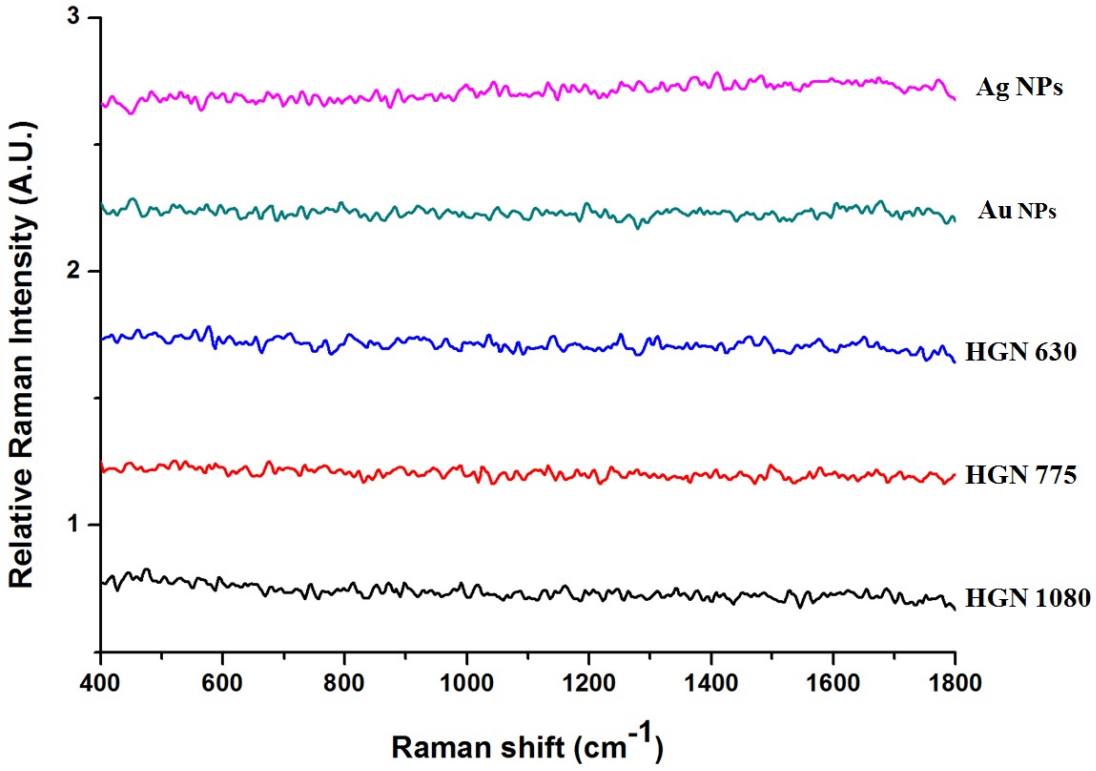

Figure S1. SERS spectra of 4,4'-azopyridine on the different types of nanoparticle suspensions, spectra recorded at 1064 nm excitation with no additional salt. HGN 650, HGN 775, and HGN 1080 mean hollow gold nanospheres with LSPRs of 650, 775, and 1080 nm respectively.

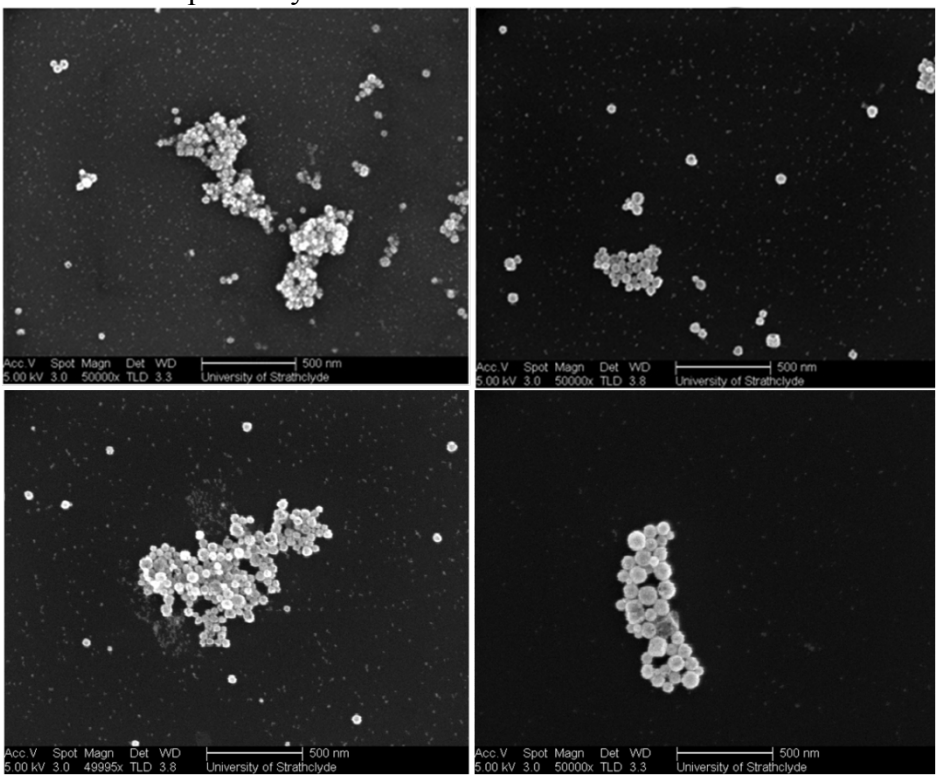

Figure S2. SEM images of different aggregates of HGN-775.

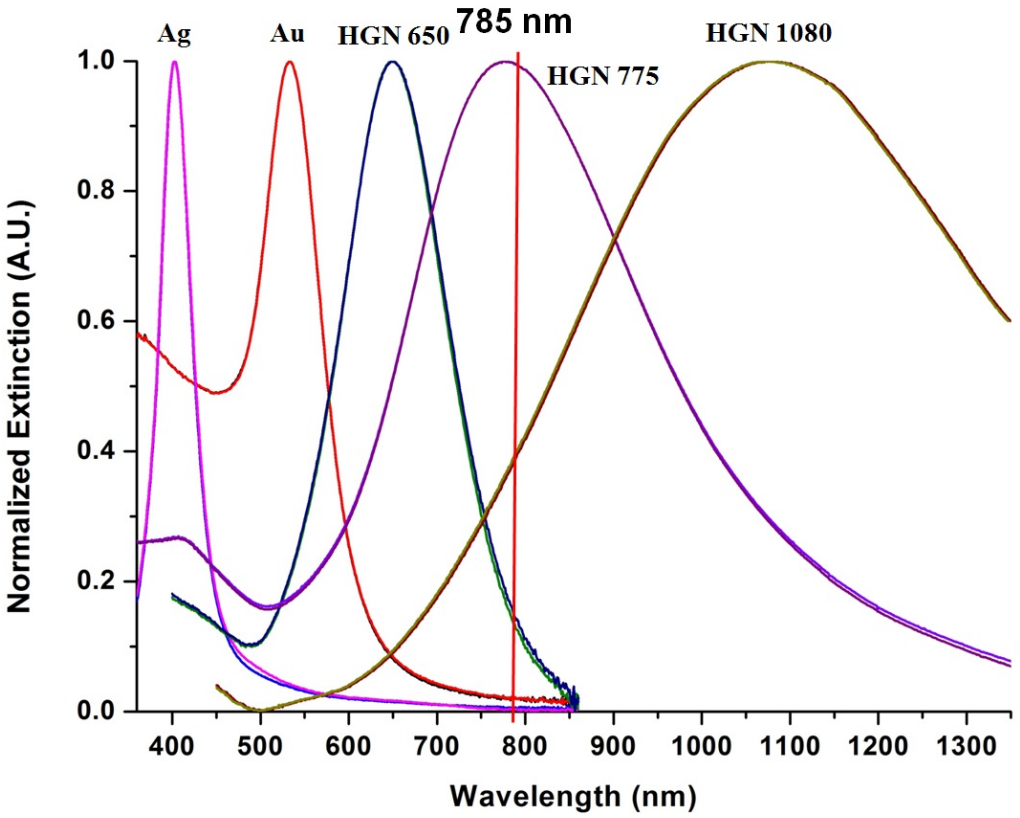

Figure S3. Normalized extinction spectra of the different types of nanoparticle suspensions before and after being illumination by a continuous 785 nm laser for 45 min. Most part of the spectra (before and after the illumination) are overlaid and there are only slight changes in the longer wavelength regions of the traces.

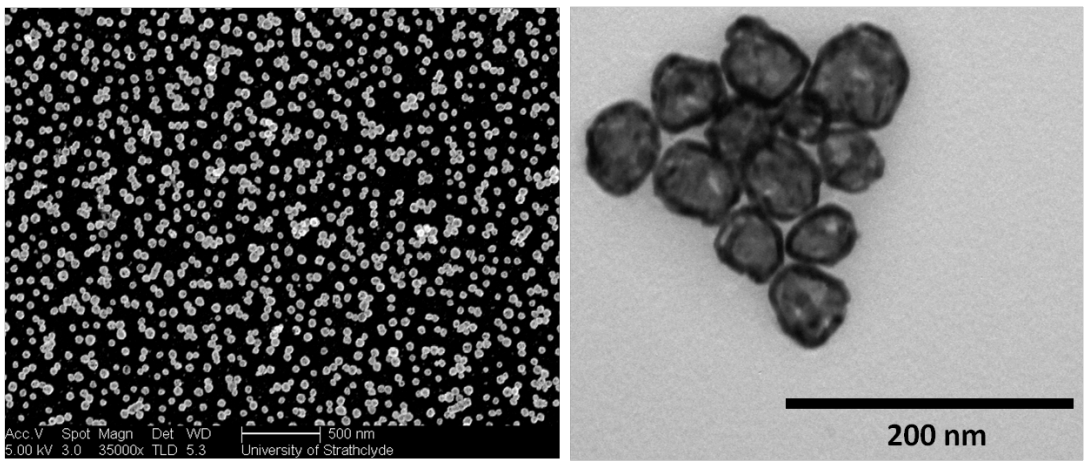

Figure S4 SEM (left) and TEM (right) images of HGN-775.

Reference:

(1)Álvarez-Puebla, R. A. *The Journal of Physical Chemistry Letters* 2012, ***3***, 857-866.