Electronic Supplementary Information

Facile synthesis of size and wavelength tunable hollow gold nanostructures for the development of a LSPR based label-free fiber-optic biosensor

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S1: Synthesis of gold seed particles

One milliliter of aqueous solution of THPC (0.96% v/v or 84 mM) was added to 45 mL of aqueous solution of sodium hydroxide (11 mM). After 5 min of vigorous stirring of the mixture, 2 mL of aqueous gold (III) chloride solution (1% w/v) was added *en masse*. The solution color immediately changed to deep brown indicating the formation of gold seeds. The resulting colloidal solution of nanoparticles was stirred for further five min and then stored at 4°C. The seed solution was characterized using UV-Vis spectroscopy and transmission electron microscopy (TEM).



Fig. S1 Extinction spectrum (a) and FEG-TEM image (b) of gold seed particles.

S2: Chemical reactions involved in the preparation diamine silver complex (DSC)

$2 \text{AgNO}_3 + 2 \text{NaOH} + 4 \text{NH}_3 \rightarrow 2 [\text{Ag}(\text{NH}_3)_2]^+ + 2 \text{NaNO}_3 + 2 \text{OH}^-$	(Net equation)
$Ag_2O + 4NH_3 + H_2O \rightarrow 2[Ag(NH_3)_2]^+ + 2OH^-$	(Step-2)
$2AgNO_3 + 2NaOH \rightarrow Ag_2O + 2NaNO_3 + H_2O$	(Step-1)



Fig. S2 Extinction spectra of silver nanoparticles produced from heteroepitaxial growth method using gold seeds.



Fig. S3 FEG-TEM image (a) and b) histogram (b) of silver nanoparticles produced from heteroepitaxial growth method using gold seeds.

Batch No.	AgNP solution (mL)	SDS solution (1 mg/mL)	Water (mL)	Volume of HAuCl4 solution taken (mL)	Concentration of HAuCl₄ solution (μM)	Molar ratio
HGNS _{0.17}	2	1	17	5	72	0.17
HGNS _{0.33}	2	1	17	5	145	0.33
HGNS _{0.50}	2	1	17	5	217	0.50
HGNS _{0.66}	2	1	17	5	289	0.66
HGNS _{1.0}	2	1	17	5	434	1.00
HGNS _{2.0}	2	1	17	5	867	2.00

Table S1: Reagents and their compositions used to produce different batches of HGNS.

S3: Method for TEM grid preparation for HGNS samples

To prepare TEM grid, first HGNS samples were purified by centrifugation method. The HGNS dispersion were centrifuged at 4000 rpm for 5 min, and the supernatant containing the dissolved silver chloride (i.e the byproduct of galvanic reaction between AgNP and gold chloride salt) and surfactant was decanted. The product was then rinsed with DI water and centrifuged for two more times, and finally re-dispersed in DI water. These purified nanostructures were dropped onto the carbon-coated copper grids and dried.

S4: Optical set-up

A dendrimer coated U-shaped fiber-optic probe was positioned with bent region of the sensor probe in a custom-made T-shaped flow cell having an inner diameter of 2.5 mm as shown in Fig. 2.8. The flow cell was used to incubate the sensing region with colloidal solution of HGNS and also to subject the probes to solution of different RI. A white light emitting diode (Edison Opto, Taiwan, model no. EDSW-1LAS-B1, spectral emission between 430 and 700 nm) was used as a light source (LS) and a portable spectrophotometer (OceanOptics Model, USB 4000) was used as a detector to monitor spectral change due to GNP binding. An objective lens (OL) ($40\times$, 0.6NA) was used to focus the light into optical fiber at input end. A fiber positioner (FP) was used to provide mechanical stability at input end of the fiber-probe. The output end of fiber probe was connected to spectrophotometer using universal bare fiber terminator (BFTU).



Fig. S4: Absorbance changes monitored at 640 nm caused by binding of GaHIgG to nonspecific Rabbit-IgG-HGNS coated U-shaped fiber probes.