Supporting Information

Self-assembled Hyperbranched Polymer - Gold Nanoparticle Hybrids: Understanding the Effect of Polymer Coverage on Assembly Size and SERS Performance

Priyanka Dey[1], Idriss Blakey[2], Kristofer J. Thurecht[2] and Peter M. Fredericks[1]

[1] School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Brisbane, Queensland 4001, Australia.
[2] Australian Institute of Bioengineering and Nanotechnology and Centre for Advanced Imaging, University of Queensland, St. Lucia, Queensland 4072, Australia.

S1: Optimization of sample concentration for TEM to minimize aggregation due to drying artefacts on the grid

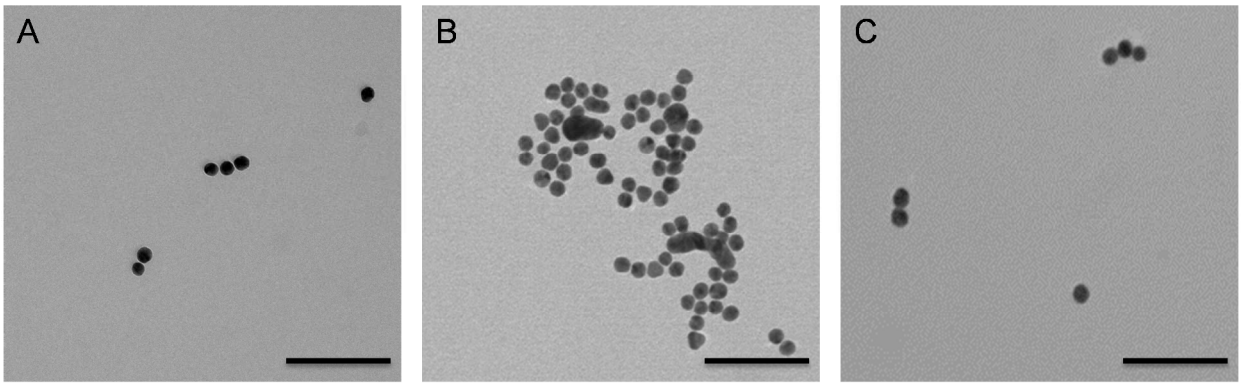


Figure S1. Comparison of Regime I hybrid with 0.1 μM HBP (A) concentrated sample by cryo-TEM (B) dilute sample (10x) by TEM (C) very dilute samples (100x) by TEM. Scale bar = 100 nm.

S2: Change in UV-vis spectra in the step-wise formation of the hybrid nano-assemblies.

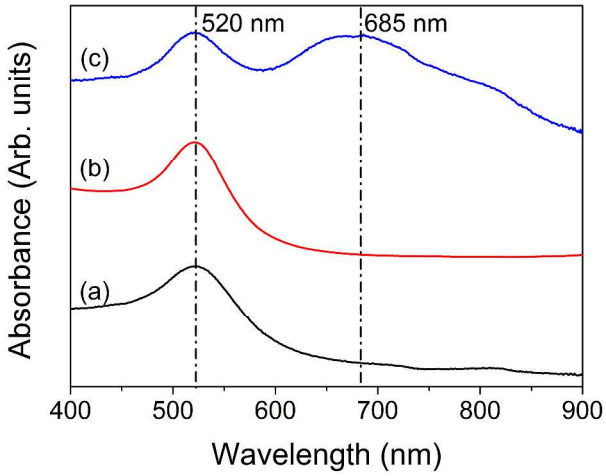


Figure S2. UV-vis spectra of (a) Citrate stabilized gold NPs with λ_{max} = 519 nm (b) Intermediate hybrids "1μM" with λ_{max} = 521 nm (c) Hybrid nano-assemblies "1μM" with primary λ_{max} = 521 nm and secondary λ_{max} = 685 nm.

S3: Dispersed gold NPs obtained with linear p(PEGMA)

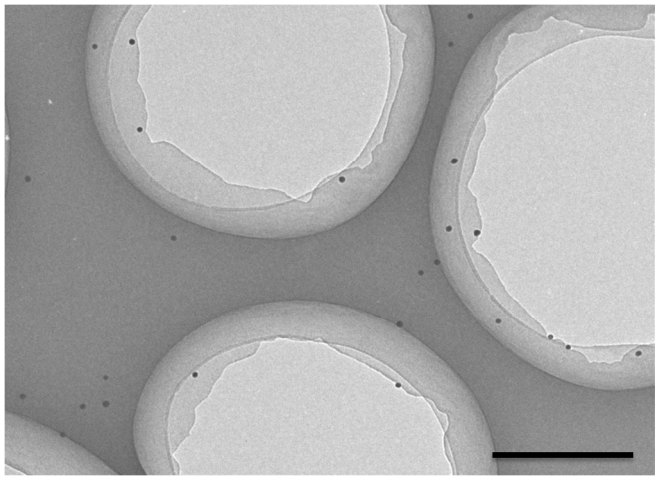


Figure S3. TEM image of gold NPs coated with linear p(PEGMA). Scale bar = 500 nm.

S4: Observation of polymer halo around NPs in hybrid nano-assemblies

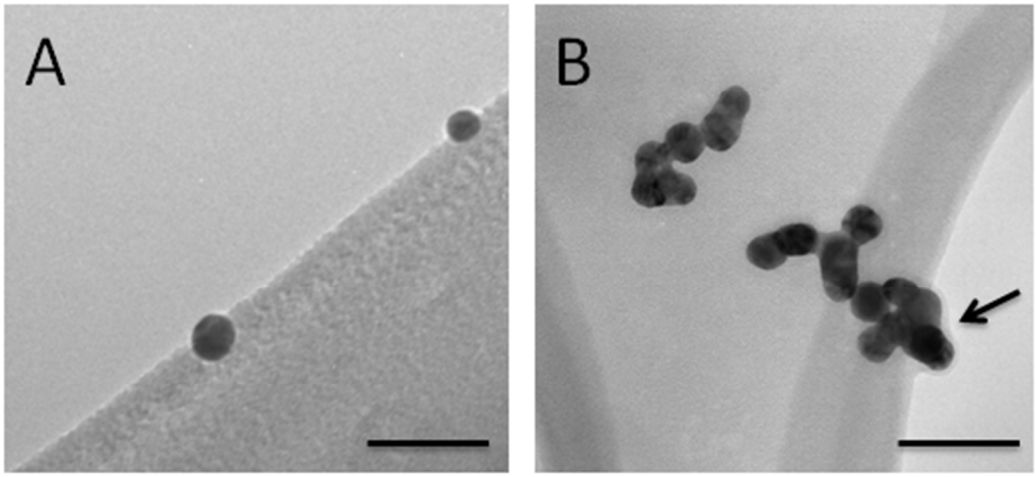
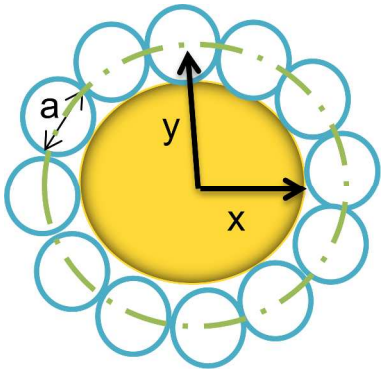


Figure S4. TEM image (A) Citrate stabilized gold NPs exhibiting no polymer halo (B) Hybrid nano-assemblies exhibiting prominent polymer halo, while NPs protrude into the holes of the holey C-coated TEM grids. Scale bar = 50 nm.

S5: Table S1. Calculation of surface coverage of the gold NPs by the hyperbranched polymers (HBP)



Where,

a = Size of HBP (nm) (DLS)

x = Radius of gold NP (nm) (TEM)

y = x + (a/2)

Considering, no overlap of adjacent HBP particles i.e., assuming a solid phase model.

For intermediate hybrids,

Total no. of HBP/gold NP for 100% surface coverage (N_{tsc})

$$= \frac{\text{Surface area at the green line at radius 'y'}}{\text{X-section area of 1 HBP particle at diameter 'a'}}$$

$$= \frac{2043.64}{56.76} = 36$$

% Surface coverage of "intermediate hybrids"

$$= \frac{\text{No. of HBP particles as per polymer concentration}}{N_{tsc}} \times 100$$

Intermediate hybrids			
	HBP conc (μM)	HBP/gold NP	% surface coverage
Regime II start	0.50	4.22 (~4)	11.71 (~ 12)%
Regime II end	2.0	16.87 (~17)	46.85 (~ 47)%

S6: Calculation of SERS enhancement factor (EF)

The SERS intensity and its error have been calculated by measuring 3 spots in a sample (in a low volume quartz cuvettes) and multiple samples of different batches. The average SERS intensity ($SERS_a$) thus calculated has been used to calculate the SERS enhancement factor (EF) for the hybrid nano-assemblies.

$$EF = \frac{\text{SERSa at 450 cm}^{-1}}{\text{Raman intensity at 450 cm}^{-1}} \times \frac{\text{Concentration of neat MB sample}}{\text{Concentration of MB in the hybrid sample}}$$