

Supporting Information

Carbazole Assay: Sodium tetraborate decahydrate (1.9 g) was dissolved in 4 ml of hot water was added dropwise to ice-cold concentrated sulfuric acid (196 ml). Next, carbazole that has been recrystallized from ethanol, (125 mg) was added to 100 ml of absolute ethanol. DAPHP standards and the samples (300 μ l) were cooled in an ice bath and 1.5 ml of the cold sulfuric acid reagent was mixed and cooled in an ice bath. This was then heated to 100 $^{\circ}$ C for 10 min, and then rapidly cooled in an ice bath. The carbazole solution (50 μ l) was added to the samples and standards, mixed, and reheated at 100 $^{\circ}$ C for 15 min. The samples were removed and put immediately into an ice bath to rapidly cool them. When at room temperature the absorbance was taken at 525 nm.

Determining DAPHP loading on to AuNPs using DTT: Au-DAPHP (100 μ l) was treated with an excess amount of DTT to displace the heparin chains. The sample was centrifuged to completely pellet the AuNPs and recover the free DAPHP. Carbazole assay was done on the supernatant, and the amount of DAPHP was estimated to be \sim 8 μ g in 100 μ l, or 3.9×10^{14} DAPHP chains.

Two different methods were used to estimate the AuNP amount within the sample. First was theoretical calculation based on the starting amount of AuCl₄.

$$\begin{aligned}\text{Amount of Au metal} &= \frac{\text{Atomic weight of Au(0)}}{\text{MW of AuCl}_4} \times \text{amount of AuCl}_4 \\ &= \frac{196.97}{393.83} \times 197 \times 10^{-6} \\ &= 9.85 \times 10^{-5} = \mathbf{98.5 \mu\text{g gold metal}}\end{aligned}$$

$$\# \text{ Au atom in } 98.6 \mu\text{g} = \frac{6.023 \times 10^{23}}{196.97} \times 98.6 \mu\text{g} = \mathbf{3.0 \times 10^{17} \text{ Au atoms}}$$

Average size of gold nanoparticles – 10 nm

$$\# \text{ Au atom/cluster} = \frac{4/3 \pi r^3}{17 \text{ \AA}} = \frac{4/3 \pi (50 \text{ \AA})^3}{17 \text{ \AA}} = \mathbf{30,784 \text{ atoms/particle}}$$

$$\# \text{ Au atom} / 98.5 \text{ \mu g} = \frac{\# \text{ Au atom in 1 \mu g}}{\# \text{ Atom/particle}} = \frac{3.0 \times 10^{17}}{30,784} = \mathbf{9.78 \times 10^{12} \text{ particles in total vol}}$$

$$\# \text{ Au particles in } 100 \text{ \mu l} = \frac{9.78 \times 10^{12}}{160 \text{ \mu l}} = \mathbf{6.11 \times 10^{12} \text{ particles}}$$

$$\# \text{ of chains / particle} = \frac{3.9 \times 10^{14} \text{ DAPHP chains}}{6.11 \times 10^{12} \text{ particles}} = \mathbf{\sim 64 \text{ chains / particle}}$$

The second method used to estimate the AuNPs concentration was developed from Haiss *et al.*¹ This method was developed to determine size and concentration of AuNPs using UV/Vis spectra. Au-DAPHP spectrum was scanned and the $A_{450 \text{ nm}} = 0.183$. The ϵ_{450} for AuNPs in the size of ~10 nm is calculated to be 6.15×10^7 . Based on $\text{conc} = A_{450 \text{ nm}} / \epsilon_{450}$, the concentration is ~60 nM. The amount of particles in 100 μl is 3.6×10^{12} .

$$\# \text{ of chains / particle} = \frac{3.9 \times 10^{14} \text{ DAPHP chains}}{3.6 \times 10^{12} \text{ particles}} = \mathbf{\sim 108 \text{ chains / particle}}$$

Reference:

- (1) Haiss, W.; Thanh, N. T. K.; Aveyard, J.; Fernig, D. G. *Anal. Chem.* (Washington, DC, U. S.) 2007, 79, 4215-4221.