Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting Information

Self-Assembly and Tunable Plasmonic Property of Gold Nanoparticles on Mercapto-Silica Microspheres

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Surface Coverage Estimation:

From the experimental result (Figure 5), the concentration ratio of TOAB capped Au particles to MPS spheres is calculated to be 8.9×10^4 to 1. According to this ratio, each gold particle occupies a surface area of 24 nm^2 on the surface of the MPS spheres. The gap between the TOAB capped gold nanoparticles is ~0.5 nm (The diameters of Au nanoparticles and MPS spheres are 5.0 and 859 nm, respectively). Using the same method, the gaps between Au particles capped with C12N and C16N are estimated to be ~2.8 and ~4.0 nm, respectively. The all-trans zigzag conformation length of the alkylthiol tail, L, can be evaluated from the empirical equation given by Bain et al. $L = 0.25 + 0.127n$, where n is the number of CH_2 groups, 0.127 is the length per $-CH_2$, and 0.25 is the part from the –SH group.[1,2] According to the data from literature,[3] the length of $C-NH_2$ is ~0.02 nm shorter than C-SH. We can then assume that the empirical equation to calculate the C12N and C16N is $L = 0.23 + 0.127n$. From this equation, the length of C12N is determined to be 1.78 nm, while the length of C16N is 2.26 nm. The gap between neighboring Au nanoparticles is shorter than double the length of an extended alkylamine chain. This discrepancy, as also being observed in previous reports, suggests that the alkyl chains might interdigitate with the chains on neighboring particles.[Ref. 26 in the main text]

References:

1. C. D. Bain, E. B. Troughton, Y. T. Tao, J. Evall, G. M. Whitesides, and R. G. Nuzzo, *J. Am. Chem. Soc.*, **1989**, *111*, 321.
2. L. Motte and M. P. Pileni, *J. Phys. Chem. B*, **1998**, *102*, 4104.
3. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 2003-2004.

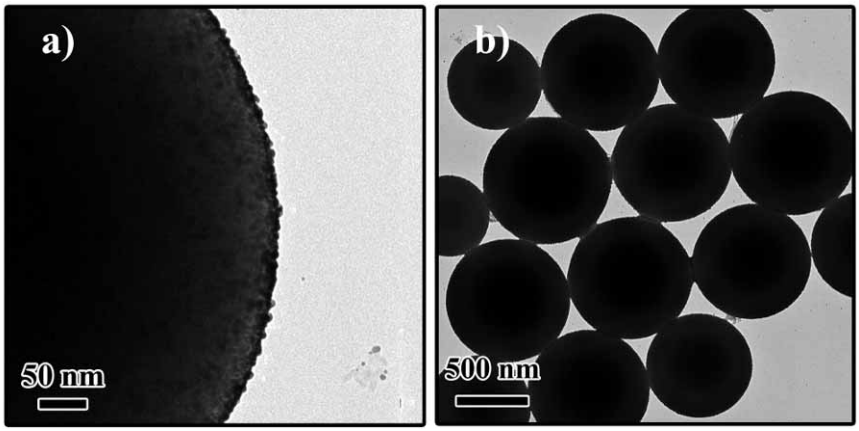

Fig. S1 a) TEM images of C12N-capped Au nanoparticles assembling on the surface of MPS spheres. b) Lower magnification image of (a).

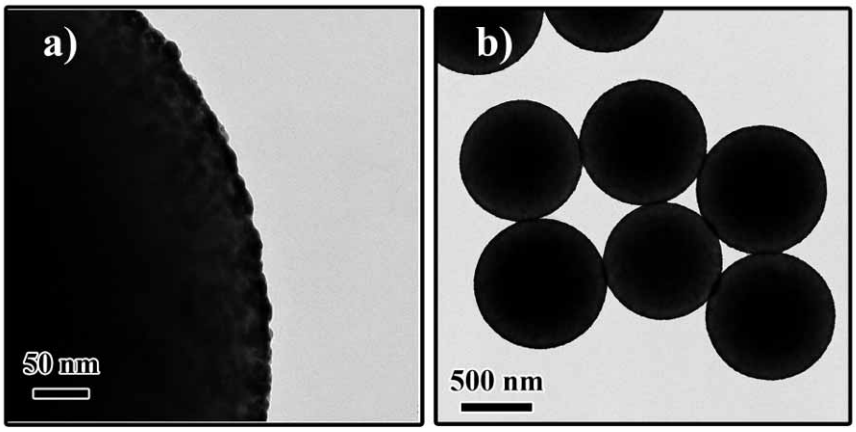

Fig. S2 a) TEM images of C16N-capped Au nanoparticles assembling on the surface of MPS spheres. b) Lower magnification image of (a).

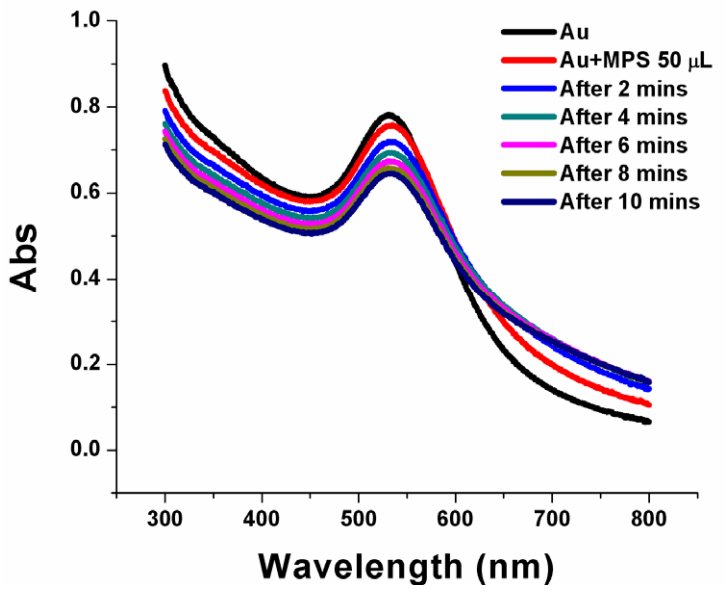

Fig. S3 The absorption spectra of TOAB-capped Au nanoparticles (2.5 mL, 8×10^{-9} mol/L) over time after MPS spheres (50 μL) were added, interval is 2 minutes. The concentration of MPS spheres is 1.5×10^{-12} mol/L.

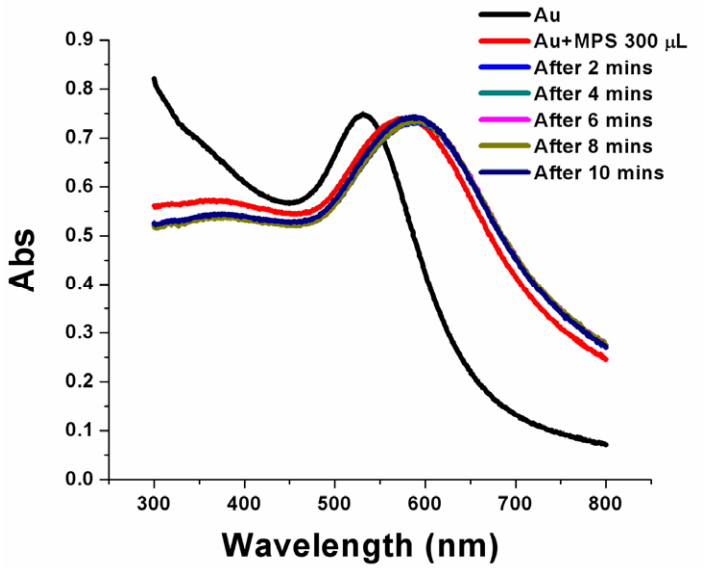

Fig. S4 The absorption spectra of TOAB-capped Au nanoparticles (2.5 mL, 8×10^{-9} mol/L) over time after MPS spheres (300 μL) were added, interval is 2 minutes. The concentration of MPS spheres is 1.5×10^{-12} mol/L.

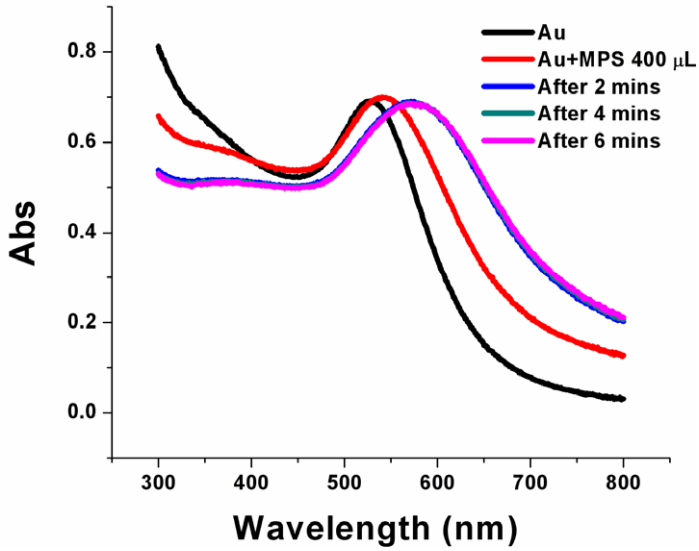

Fig. S5 The absorption spectra of TOAB-capped Au nanoparticles (2.5 mL, 8×10^{-9} mol/L) over time after MPS spheres (400 μL) were added, interval is 2 minutes. The concentration of MPS spheres is 1.5×10^{-12} mol/L.

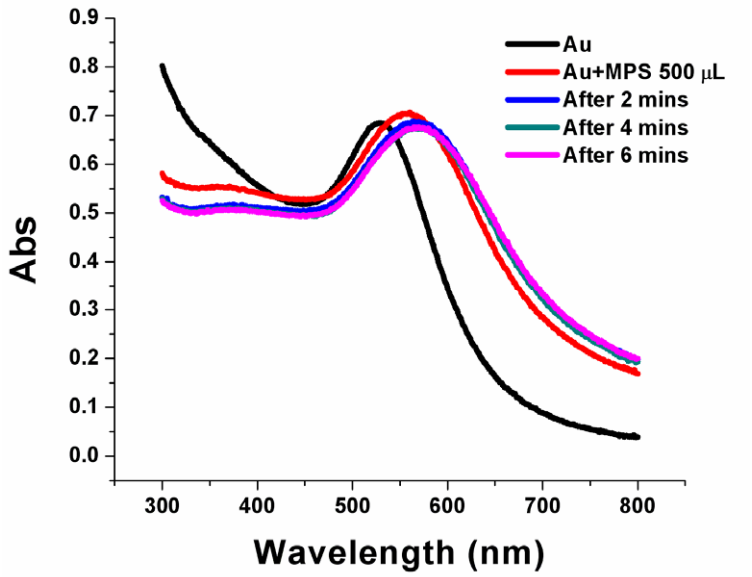

Fig. S6 The absorption spectra of TOAB-capped Au nanoparticles (2.5 mL, 8×10^{-9} mol/L) over time after MPS spheres (500 μL) were added, interval is 2 minutes. The concentration of MPS spheres is 1.5×10^{-12} mol/L.

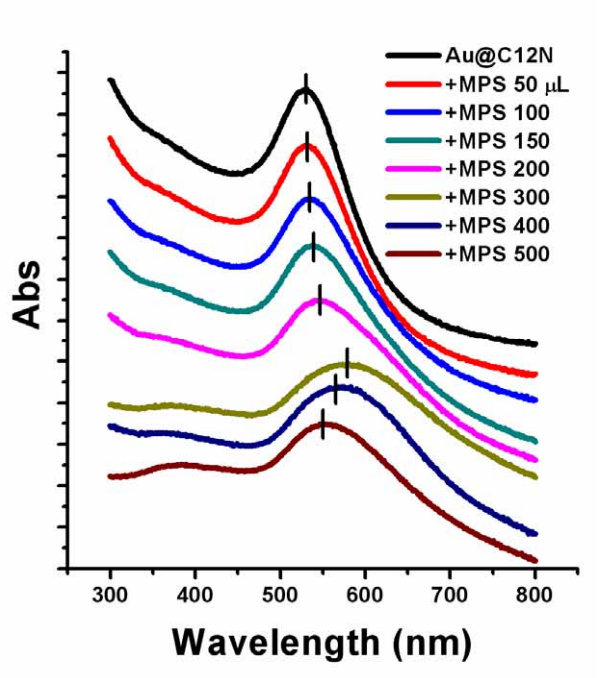

Fig. S7 Concentration effect of MPS spheres on the absorption spectra of C12N-capped Au nanoparticles in toluene. From top to bottom the volume of MPS sphere solution is 0, 50, 100, 150, 200, 300, 400 and 500 μL. Each spectrum was taken after assembly achieved equilibrium.

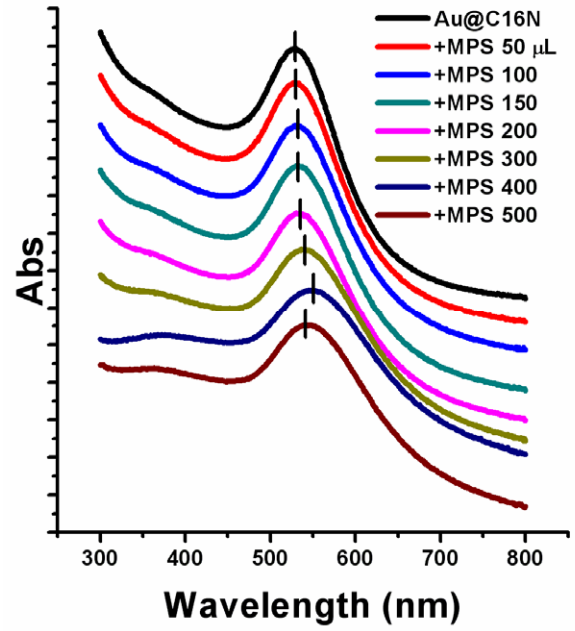

Fig. S8 Concentration effect of MPS spheres on the absorption spectra of C16N-capped Au nanoparticles in toluene. From top to bottom the volume of MPS sphere solution is 0, 50, 100, 150, 200, 300, 400 and 500 μL. Each spectrum was taken after assembly achieved equilibrium.