

Electronic Supplementary Information

Combined experimental and simulation study of self-assembly
of colloidal gold nanoparticles on silanized glass

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1. Synthesis of Au nanoparticles of size ~ 40 nm by following the method reported by Sai *et al.* [1].

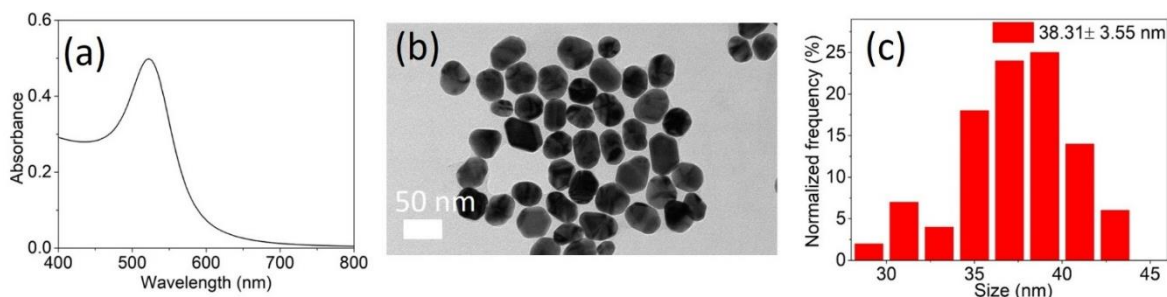


Figure S1. (a) UV-VIS absorption spectrum (b) TEM image and (c) size distribution of synthesized Au NPs.

2. Synthesis of Au nanoparticles of different size ranging from 14 nm to 100 nm.

A seed-mediated protocol suggested by Bastus *et al.* was employed for the synthesis of Au NPs of different sizes.[2]

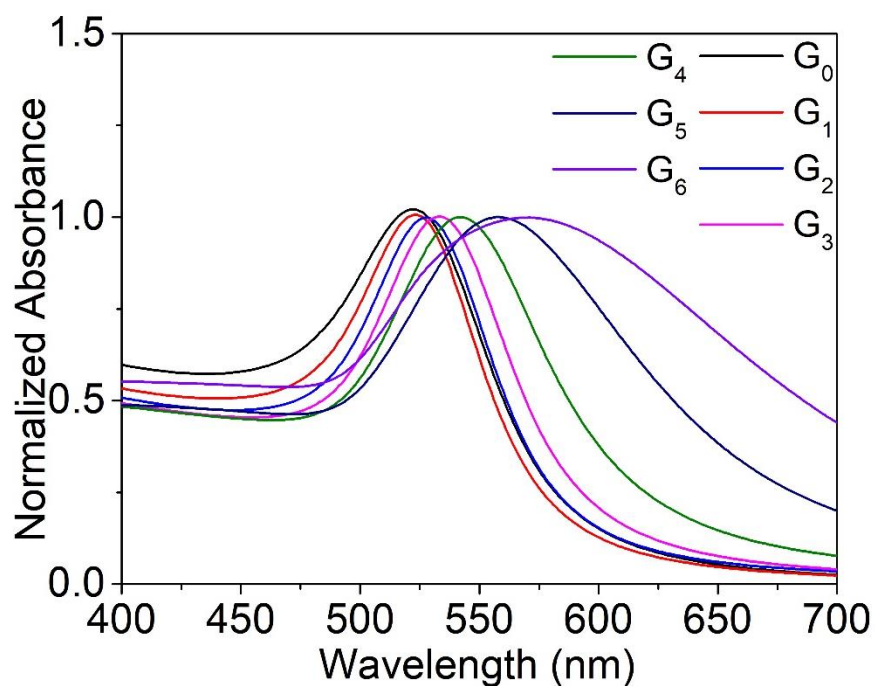


Figure S2. UV-VIS absorbance spectra of Au NPs of different size synthesized via seed-mediated method. $G_0 = 14.65 \pm 1.85$ nm, $G_1 = 24.41 \pm 3.43$ nm, $G_2 = 34.79 \pm 4.58$ nm, $G_3 = 48.42 \pm 5.31$ nm, $G_4 = 63.23 \pm 7.65$ nm, $G_5 = 77.32 \pm 7.14$ nm, and $G_6 = 101.81 \pm 10.31$ nm.

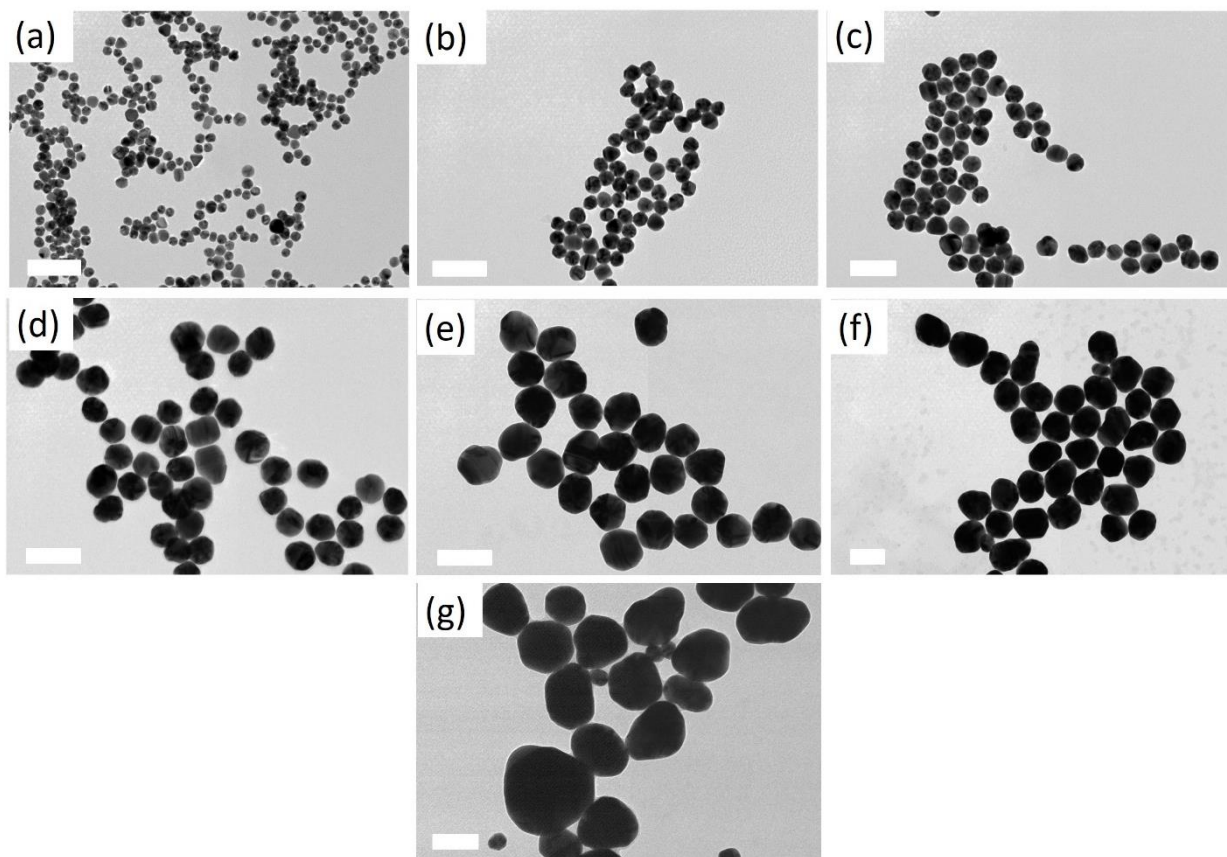


Figure S3. TEM images of Au NPs of different size synthesized via seed-mediated method. (a) 14.65 ± 1.85 nm (G_0), (b) 24.41 ± 3.43 nm (G_1), (c) 34.79 ± 4.58 nm (G_2), (d) 48.42 ± 5.31 nm (G_3), (e) 63.23 ± 7.65 nm (G_4), (f) 77.32 ± 7.14 nm (G_5), and (g) 101.81 ± 10.31 nm (G_6). Scale bars =100 nm.

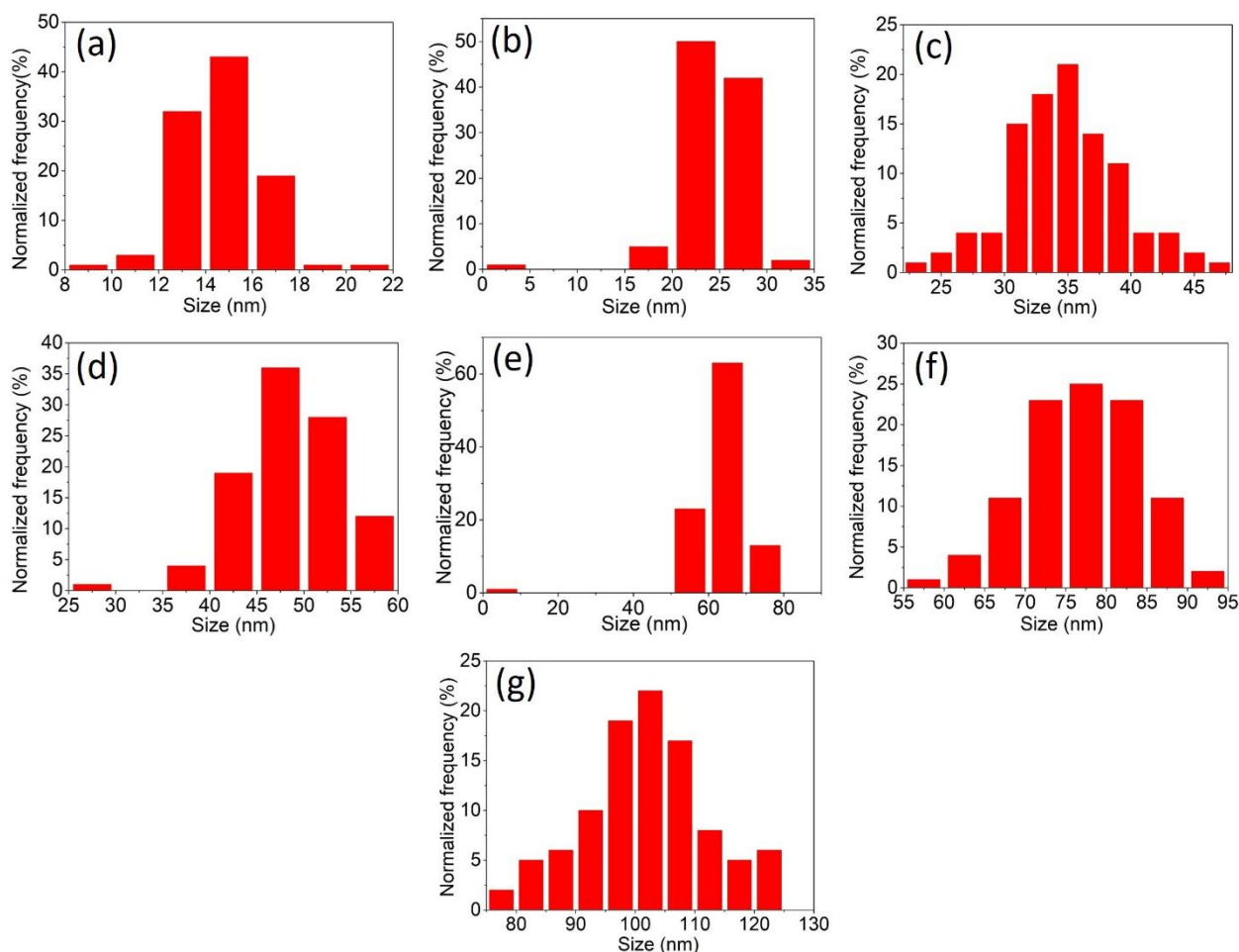


Figure S4. Size distribution of Au NPs of different size synthesized via seed-mediated method. (a) 14.65 ± 1.85 nm (G_0), (b) 24.41 ± 3.43 nm (G_1), (c) 34.79 ± 4.58 nm (G_2), (d) 48.42 ± 5.31 nm (G_3), (e) 63.23 ± 7.65 nm (G_4), (f) 77.32 ± 7.14 nm (G_5), and (g) 101.81 ± 10.31 nm (G_6).

3. Bulk concentration of Au NP in dispersion.

The concentration of AuNP dispersion is calculated by using the given below equation with the knowledge of solution absorbance,

$$A_{liquid} = \frac{C_{Au} l \epsilon}{N_{Av}} \text{ ----- S1}$$

where A_{liquid} , C_{Au} , l , ϵ and N_{Av} represent absorbance of Au nanoparticle's dispersion, the concentration of Au NP dispersion (moles/ml), optical path length (10 mm), and molar extinction coefficient of Au NPs ($M^{-1}cm^{-1}$) and Avogadro number respectively. The molar extinction coefficient of Au NP was taken from the datasheet provided by Sigma-Aldrich. [3]

4. Adsorption of APTMS on silica substrates.

Surface roughness measurement of APTMS coated and uncoated portion on the same glass slide indicates the adsorption of APTMS on silica surface. The uncoated region of silica reported a surface roughness of 0.55 nm whereas APTMS coated region reported 1.63 nm. The difference in surface roughness between the coated and uncoated portion implies the adsorption of APTMS.

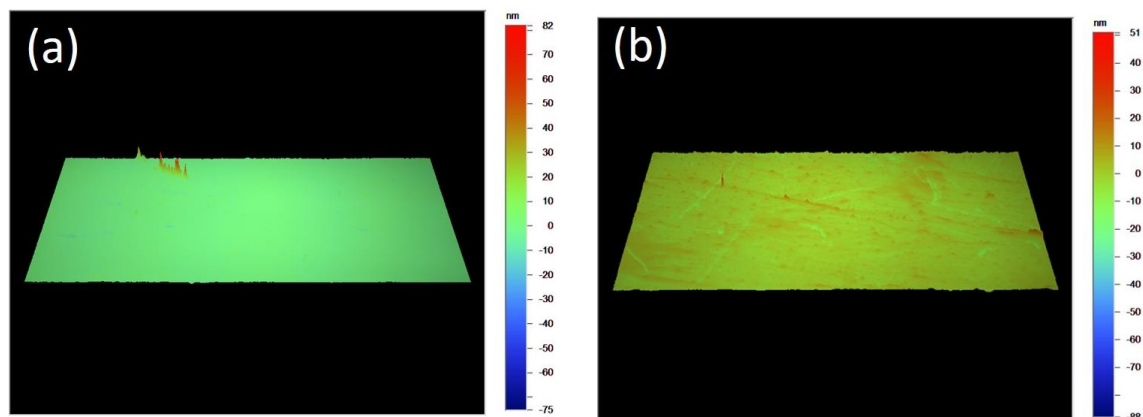


Figure S5. Surface roughness measurement of APTMS coating on silica substrate (a) uncoated and (b) coated silica.

5. Water contact angle measurements of substrates.

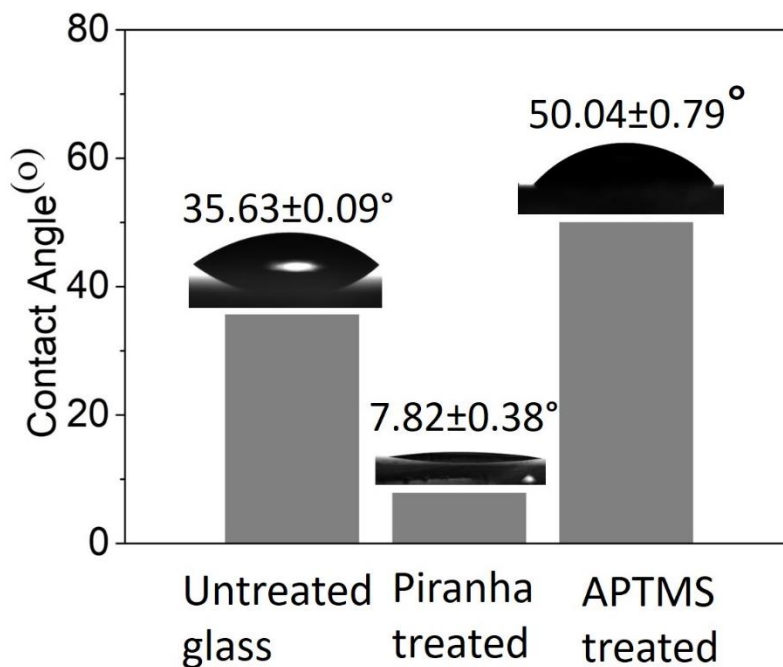


Figure S6. Water contact angles were measured on bare glass, piranha treated glass, and APTMS-modified glass.

6. Au NP monolayer formation on APTMS modified silica substrate

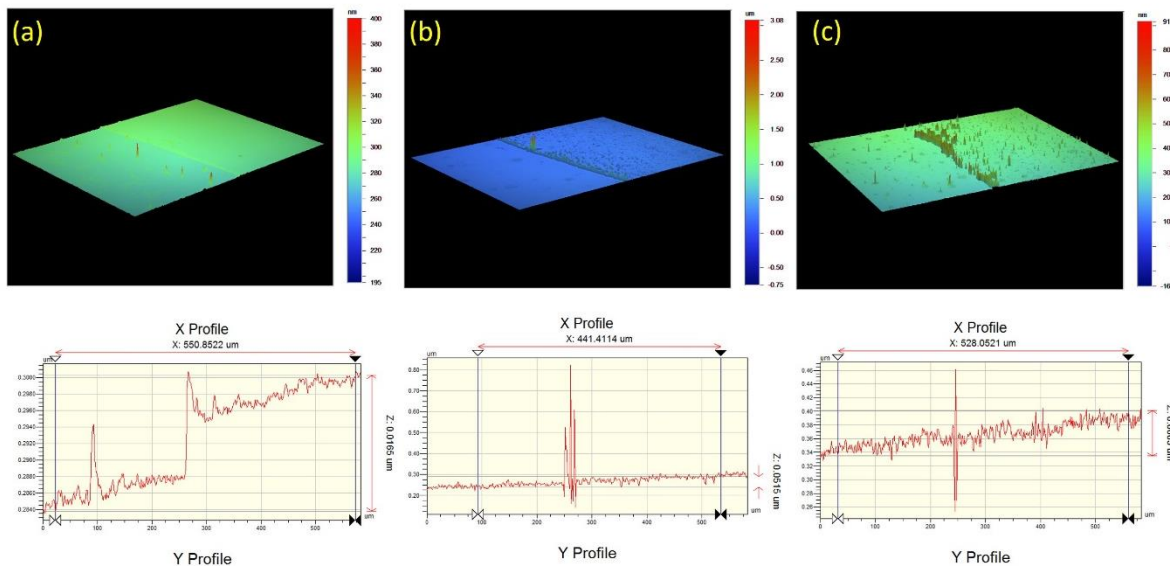


Figure S7. Surface profilometry of Au NP coated silane modified surface. (a) $G_0 = 14.65 \pm 1.85$ nm (b) $G_3 = 48.42 \pm 5.31$ nm, and (c) $G_4 = 63.23 \pm 7.65$ nm.

SEM images of Au NP coated glass substrates reveal that Au NPs are uniformly distributed on the modified surface, not arranged one up on the other. Moreover, the surface profilometry and surface roughness measurements of Au NP coated silane-modified substrates also support the monolayer formation. The surface profilometry and surface roughness measurements of Au NP ($G_0 = 14.65 \pm 1.85$ nm, $G_3 = 48.42 \pm 5.31$ nm, and $G_4 = 63.23 \pm 7.65$ nm) coated substrates are shown in Figure S7. As the measured film thickness approximately matches the size of the coated Au NP, it implies Au NP monolayer formation on the substrate. The corresponding surface roughness is measured as 5.83 nm, 26.56 nm, and 30.96 nm respectively. The increased surface roughness with Au NP size is also considered an indication of monolayer formation.

7. Simulation-based substrate occupancy.

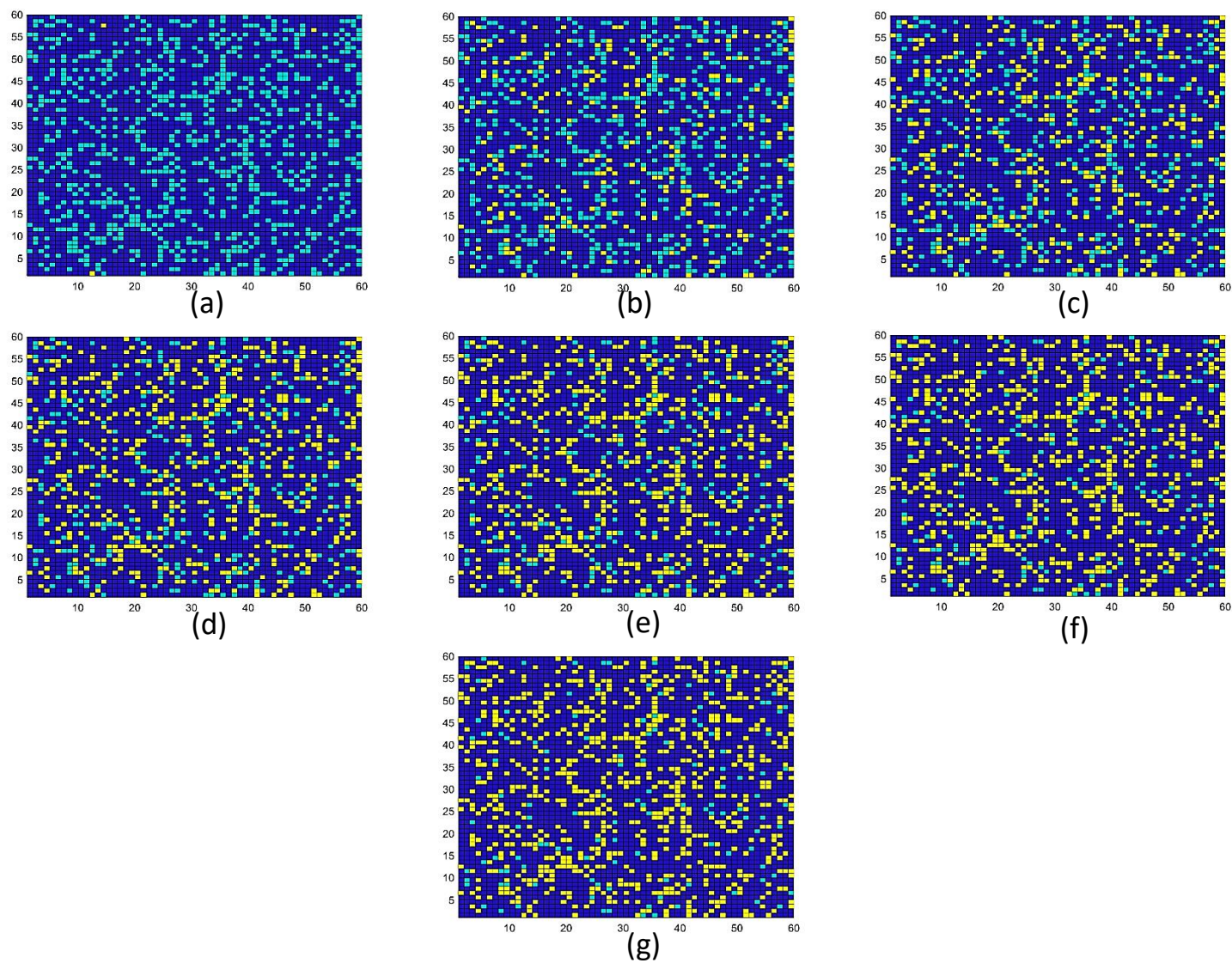


Figure S8. Visualization of nanoparticle concentration on the substrate with increasing number of iterations, (a) 1, (b) 100, (c) 200, (d) 300, (e) 400, (f) 500, (g) 600, yellow representing nanoparticle trapped functional group, light blue representing vacant functional group and dark blue representing the points without functional groups.

8. Analysis of adsorption isotherm for Au NPs deposition on silanized glass substrates.

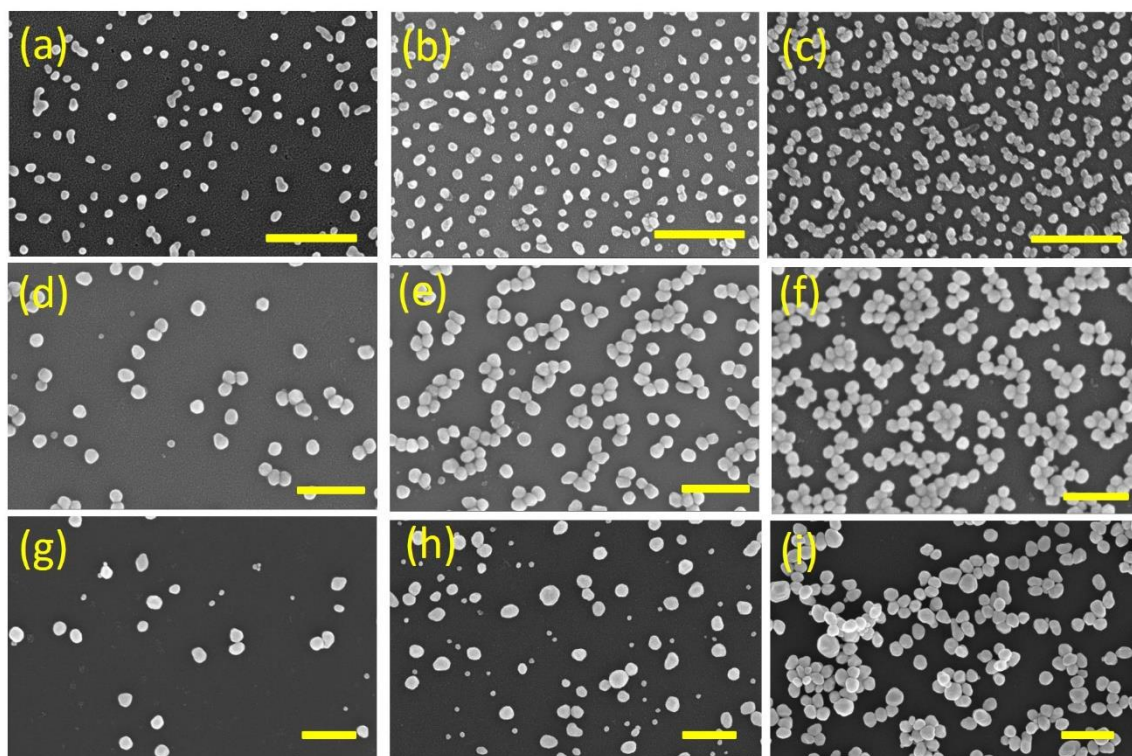


Figure S9. SEM images of Au NP deposition on silanized glass substrates with varying bulk concentration. (a) – (c): Au NP of size: -38.31 ± 3.55 nm, (a) 0.11 nM, (b) 0.54 nM, and (c) 1.07 nM. (d) – (f): Au NP of size: -77.31 ± 7.14 nm, (d) 0.76×10^{-2} nM, (e) 5.31×10^{-2} nM, and (f) 11.5×10^{-2} nM. (g) – (i): Au NP of size: -101.81 ± 10.31 nm, (d) 2×10^{-3} nM, (e) 10×10^{-3} nM, and (f) 80×10^{-3} nM. APTMS concentration used: - 11 mM. Scale bars =500 nm.

9. Relation between the probability of a NP being adsorbed on the modified substrate and bulk concentration.

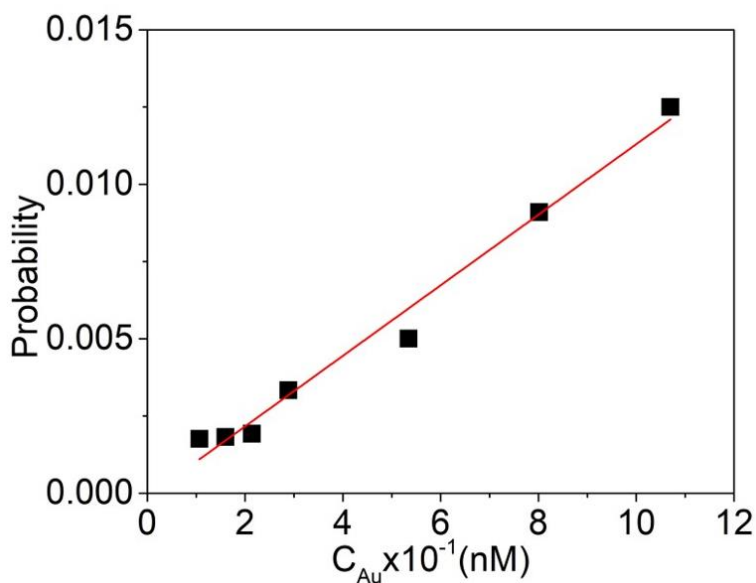


Figure S10. The probability of nanoparticles being trapped by a functional group vs bulk concentration (C_{Au}). Deposition of Au NP of size 38.31 ± 3.55 nm with different bulk concentrations ranging from 0.11 - 1.07 nM was considered.

10. Effect of Au NP size

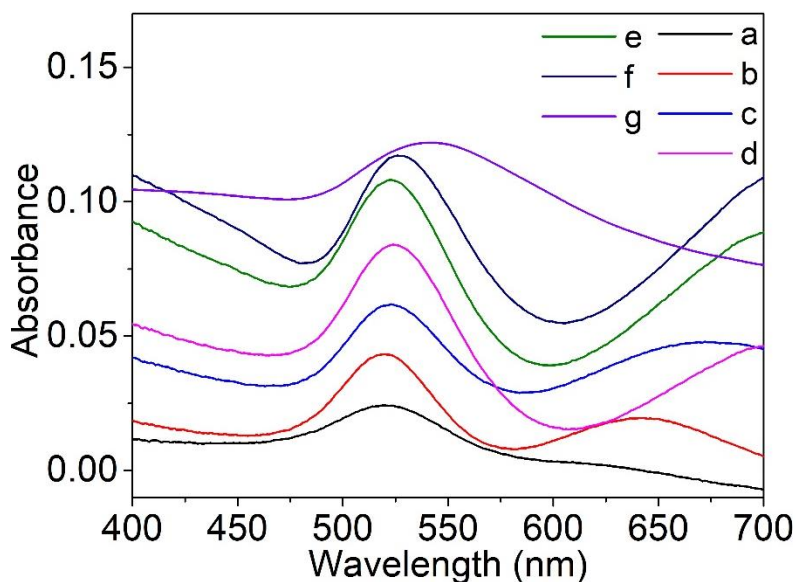


Figure S11. UV-VIS absorbance spectra of Au NPs of different sizes were deposited on silanized glass substrates. (a) 14.65 ± 1.85 nm, (b) 24.41 ± 3.43 , (c) 34.79 ± 4.58 , (d) 48.42 ± 5.31 , (e) 63.23 ± 7.65 , (f) 77.32 ± 7.14 and (g) 101.81 ± 10.3 nm. Bulk concentration of NP fixed at 0.02 nM (1.14×10^{10} NP mL⁻¹). APTMS concentration = 1 mM.

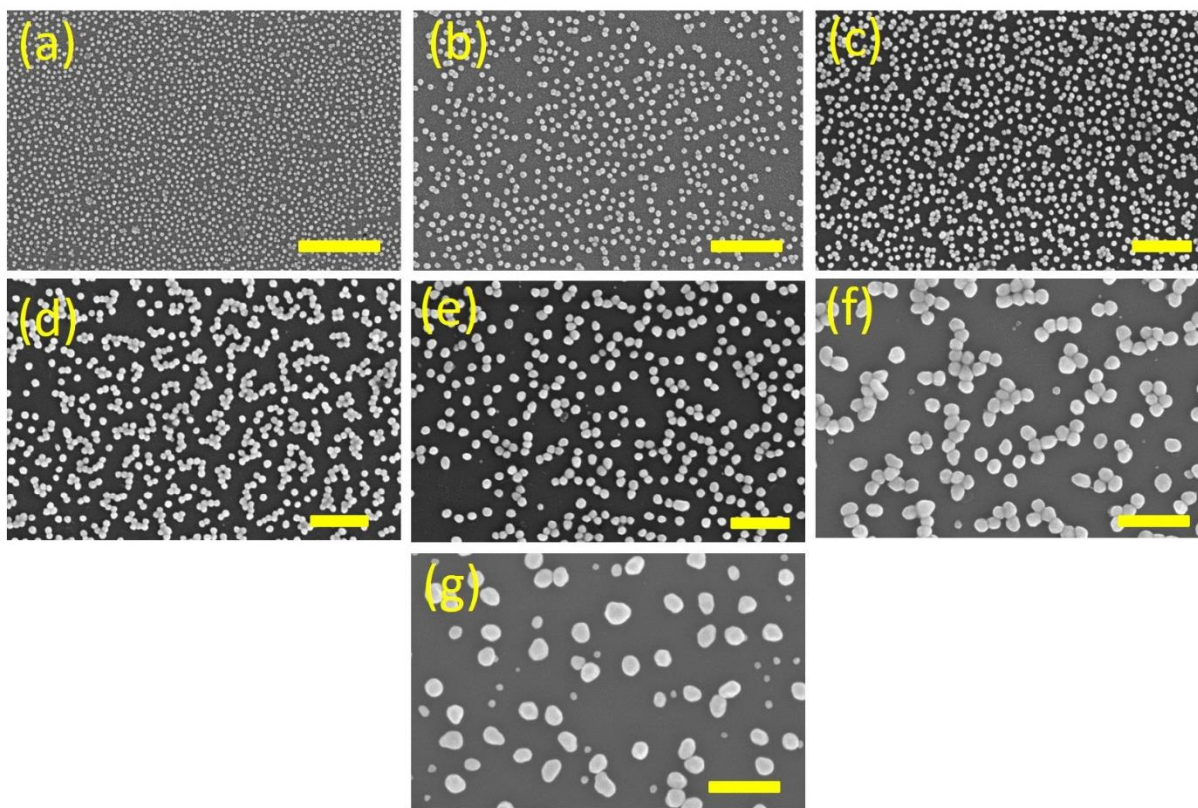


Figure S12. SEM images of Au NPs of different size deposited on silanized glass substrates. (a) 14.65 ± 1.85 nm, (b) 24.41 ± 3.43 , (c) 34.79 ± 4.58 , (d) 48.42 ± 5.31 , (e) 63.23 ± 7.65 , (f) 77.32 ± 7.14 and (g) 101.81 ± 10.3 nm. Nanoparticle bulk concentration = 0.02 nM (1.14×10^{10} NP mL⁻¹). APTMS concentration = 11 mM. Scale bars = 500 nm.

References: -

1. V.Sai, T. Kundu and Mukherji, *Biosensors and Bioelectronics*, 2009, **24**, 2804–2809.
2. N.G Bastus, J. Comenge and Puentes, *Langmuir*, 2011, **27**, 11098–11105.
3. X.Liu, M. Atwater, J.Wang and Huo, *Colloids and Surfaces B: Biointerfaces*, 2007, **58** 3-7.