Supporting information for

A Facile and Efficient Method to Modify Gold Nanorods with Thiolated DNA at Low pH Value

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Experimental section

Chemicals and Materials

Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \cdot 3H_2O$), Hexadecyltrimethyl ammonium bromide (CTAB), Sodium dodecyl sulfate (SDS), Tris (2-carboxyethyl) phosphine hydrochloride (TCEP), Bis (*p*-sulfonatophenyl) phenyl phosphine dihydrate dipotassium salt (BSPP), Silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), L-ascorbic acid, trisodium citrate dihydrate (SC), Citric acid (CA) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. Thiolated oligonucleotides were purchased from Invitrogen.

Synthesis and purification of gold nanorod:

The synthesis of AuNRs was carried out using the silver-assisted seed-growth procedure adapted from literature [1].

a. GNP seed synthesis

First, 50 µL of 50 mM $HAuCl_4$ was added into 10ml of 0.1 M CTAB aqueous solution and vortexed vigorously. Then, 0.6 ml 10mM fresh prepared ice cold $NaBH_4$ was added to the mixture while stirring vigorously. The solution color changed to yellowish brown immediately. The resulting solution consists of AuNP seeds, which act as nucleation points for AuNR growth.

b. GNR synthesis

80 µL of 50 mM $HAuCl_4$ solution was added into 10 mL of 0.1 M CTAB solution. Then, 80µL of 10 mM $AgNO_3$ solution was added. After gentle mixing, 50 µL of 100 mM ascorbic acid solution was added and mixed thoroughly. To this mixture, 17 µL of the previously prepared AuNP seed solution was added. The mixture was kept undisturbed for several hours until the solution turned purple which indicated the formation of AuNR. AuNR solution was centrifuged (15 mins, 7000 rpm), the supernatant was discarded and the pellet was suspended in 1000 µL of nanopure water. 500 µL of AuNRs solution was washed twice by centrifugation and re-suspension in nanopure water. The AuNRs concentration was measured using UV-Vis spectra (Figure S1).

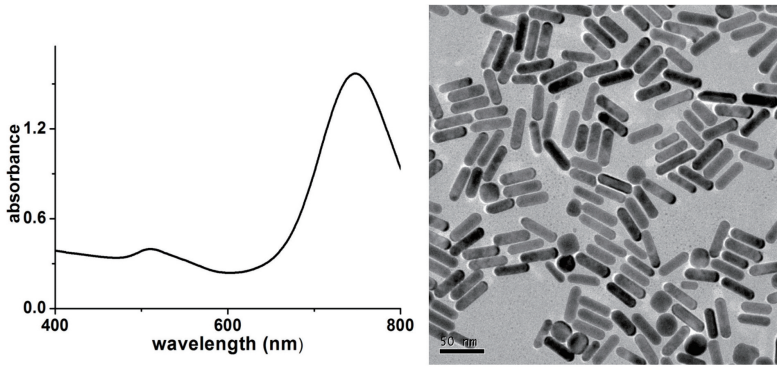

Figure S1. UV-vis spectrum (left) and TEM image (right) of new freshed GNR. Scale bar is 50 nm.

Preparation of DNA functionalized AuNRs:

a. Preparation of the Thiolated DNA

The S-S bond in thiolated DNA obtained from Invitrogen was reduced by adding 60 µL of 100 mM TCEP (tris (2-carboxyethyl) phosphine) to 600 µL of 100 µM DNA solution and incubated for two hours. Excessive TCEP was removed using a G25 spin column (GE Healthcare).

b. Coating of DNA on AuNR

Traditional aging method to modify GNR is complicated and time-consuming. The process of RMLP method is very simple. Firstly, 1X TBE and 0.1% SDS was mixed together and shaked gently. HCl was used to adjust mixture pH to be 3.0. Then the purified DNA-AS1 was added to this mixture. Lastly, newly synthesized GNR without over growth was added to the solution. After several minutes, the mixture was centrifuged (20 mins, 7000 rpm) for three times, the supernatant was discarded and the pellet was suspended in 1X TBE (100 mM NaCl).

Synthesis of GNP

15nm GNP was synthesized by using SC (trisodium citrate dihydrate) to reduce $HAuCl_4$. 160 µl of 50mM $HAuCl_4$ was added to 50 ml nanopure water and heated to boiling. Then 2ml of TSC (1% SC, 0.05% CA) was added to this mixture. The solution was set on vigorous stirring for 15 minutes then cooled down to room temperature and centrifuged (20 mins, 6000 rpm) to remove excess TSC. The pellet was re-dispersed in nanopure water. The GNPs concentration was measured using UV-Vis spectra (Figure S2).

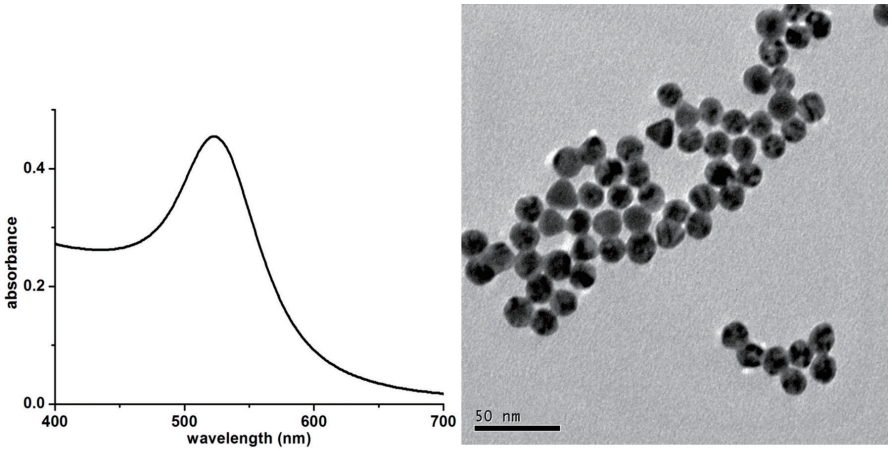

Figure S2. UV-vis spectrum (left) and TEM image (right) of fresh prepared GNP. Scale bar is 50 nm.

Preparation of DNA functionalized AuNPs:

a. Phosphination of AuNPs

AuNPs were stabilized with absorption of Bisp-sulfonatophenyl-phosphene dihydrate dipotassium salt (BSPP). Phosphine coating increases the negative charge on the particle surface, therefore, stabilizes the AuNPs in high electrolyte concentrations at a higher particle density. BSPP (17 mg) was added to the colloidal nanoparticle solution and the mixture was shaken overnight at room temperature. Sodium Chloride (solid) was added slowly to this mixture while stirring until the color changed from deep burgundy to light purple. The resulting mixture was centrifuged at 3000 rpm for 30 min and the supernatant was carefully removed with a pipette. AuNPs were then suspended in 1 mL solution of BSPP (2.5 mM). Upon mixing with 1 mL methanol, the mixture was centrifuged, the supernatant was removed and the AuNPs were re-suspended in 1 mL BSPP solution (2.5 mM). The concentration of the AuNPs was estimated using UV-vis spectrometer.

b. Preparation of DNA functionalized AuNPs

The AS2-DNA which is complementary to AS1 were incubated with an equimolar ratio of phosphinated AuNPs in 1xTBE buffer (89 mM Tris, 89 mM boric acid, 2 mM EDTA, pH 8.0) containing 50 mM NaCl for overnight at room temperature. The concentration of salt was added to 500 mM over 24 hours. The mixture was centrifuged (20 mins, 6000 rpm) for three times and re-dispersed in 1X TBE (100 mM NaCl).

Assembly of GNR and GNP, and gel electrophoresis purification

AS1-GNR and AS2-GNP was mixed together in 1X TBE buffer (100 mM NaCl). The ratio of GNP to GNR is 20:1. The mixture was annealed in PCR from 45℃ to 25℃ over 12 hours. The mixture was loaded in 1.0% agarose and run for 15 minutes (90 V). There were several bands in the agagrose gel image. The fastest band which was the excess GNPs was abandoned. We assumed that the second fast band was the target satellite nanostructures. The target band was extracted from gel through electro-elution.

TEM images of GNR-GNP satellite structures.

TEM samples were prepared by dropping 10μL of the purified sample solution on a carbon-coated grid. After 5 minutes, the sample drop was wicked away from the grid by filter paper. The grid was washed by a drop of water to remove the excess salt, and the excess water was again wicked away by filter paper. The grid was kept at room temperature to allow drying.

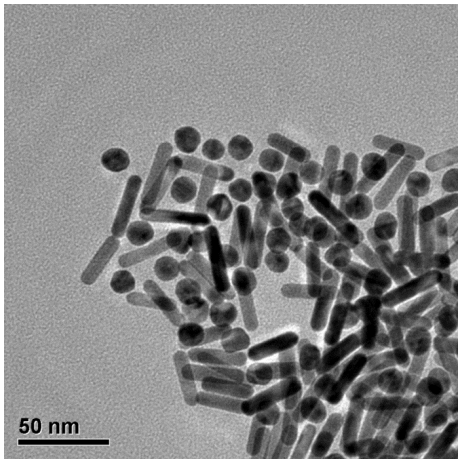

Figure S3.TEM image of assembly product from AS1-GNR and random DNA capped GNP. Scale bar is 50 nm.

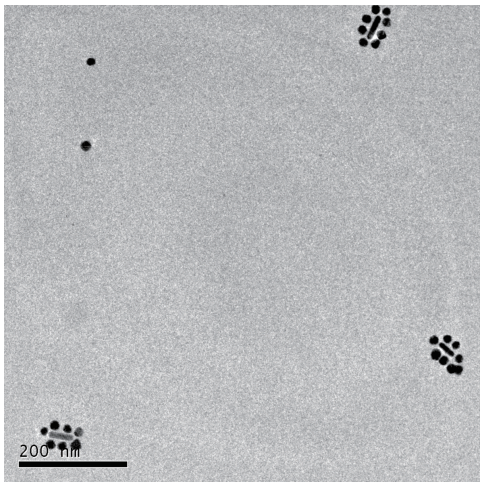

Figure S4. TEM image of GNR-GNPs satellite nanostructures. Scale bar is 200 nm.

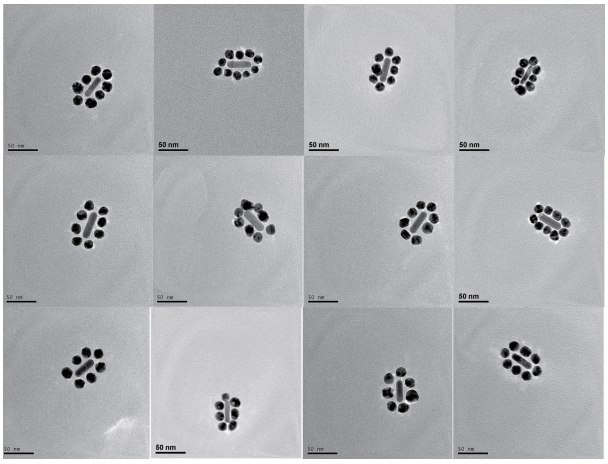

Figure S5. Additional TEM images of GNR-GNPs satellite nanostructures. Scale bar is 50nm.

Reference

1. B. Nikoobakht and M. A. El-Sayed, Chem. Mater. 2003, **15**, 1957