Electronic Supplementary Information (ESI)

THREADING DIFFERENT METAL NANOMATERIALS ON NATURAL PHIX174 DNA TO ASSEMBLE A NECKLACE

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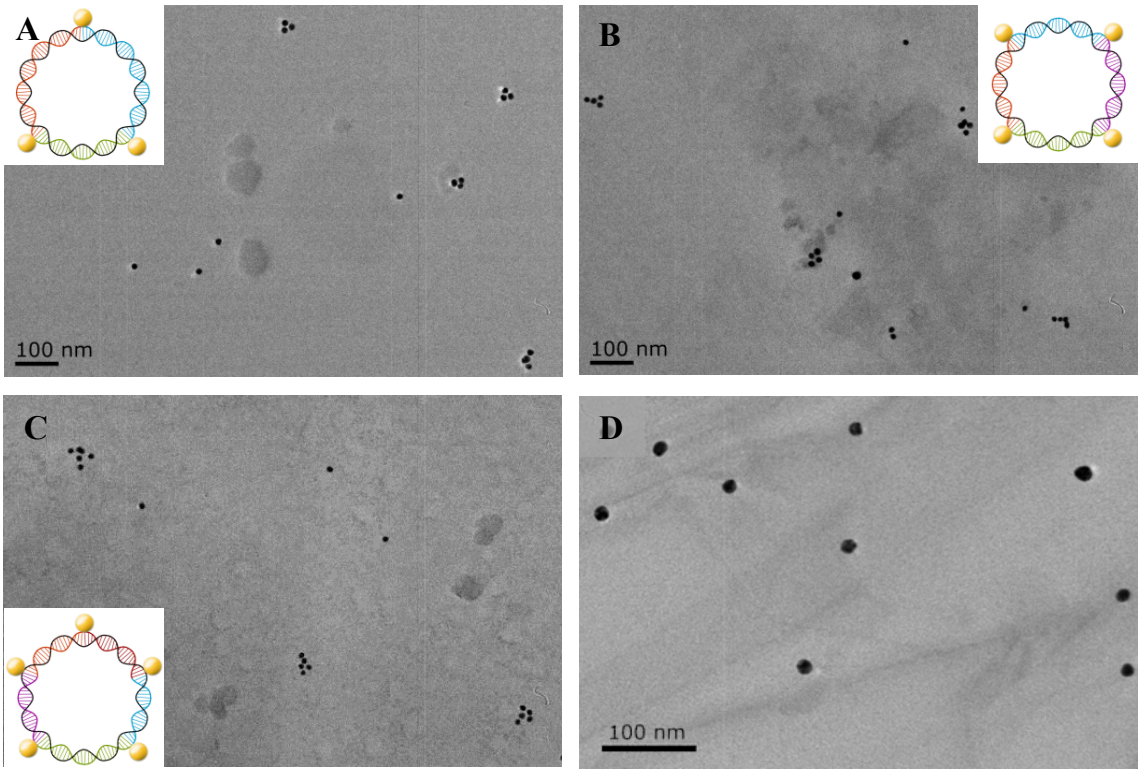
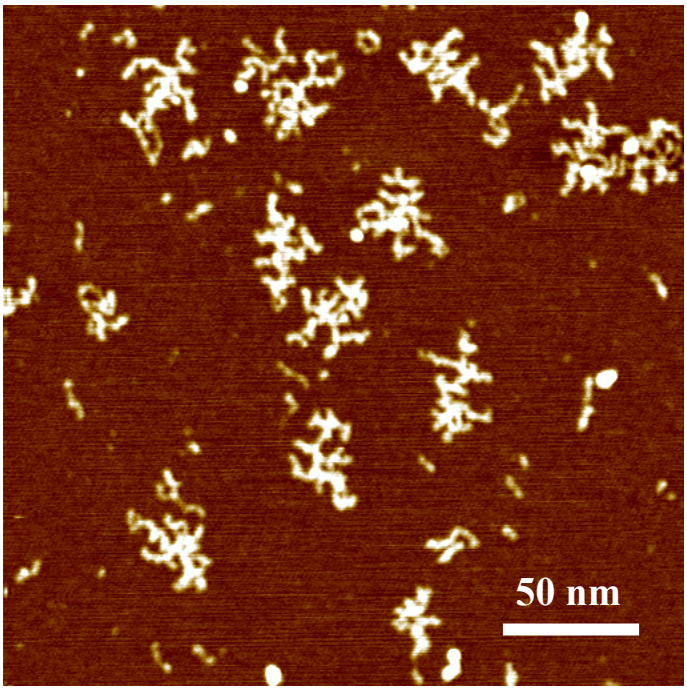
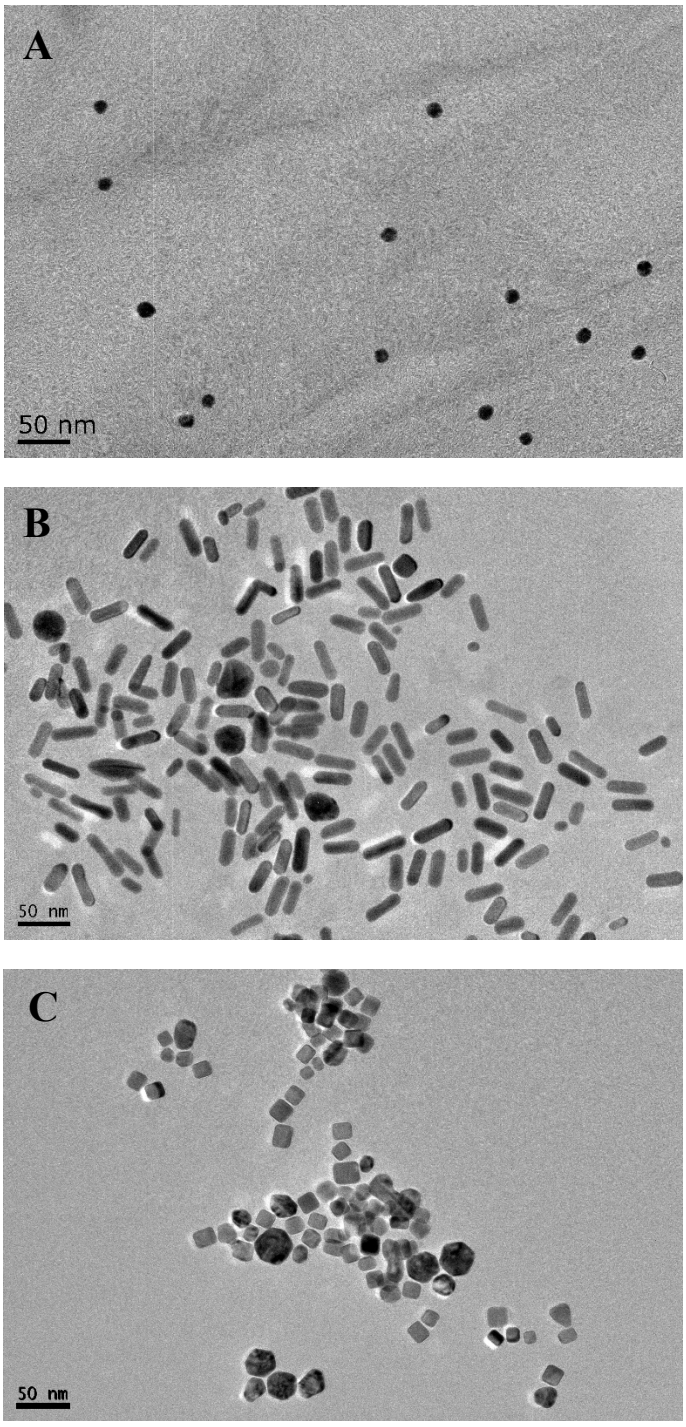


Supplementary Figure S1. TEM images of AuNPs-DNA necklace with different numbers AuNPs assembled on PhiX174 DNA motif. (A) Three AuNPs assembled on DNA motif showing similar triangle structure or the linear structure. (B) Four AuNPs organized on DNA motif and TEM images showed the similar square structure or linear structure. (C) Five nanoparticles organized in DNA motif. (D) TEM images showed all gold nanoparticles were isolated in the control group where no polymerase was added during the PCR process.



Supplementary Figure S2. AFM image of PhiX174 shows that the DNA is seriously compact and the diameter of each DNA structure is approximately 100 nm.



Supplementary Figure S2. TEM images of (A) gold nanoparticles (AuNPs), (B) gold nanorods (AuNRs) and (C) palladium nanocubes (PdNCs).

EXPERIMENTAL SECTION

Materials.

The oligonucleotide primers were designed by the software of Primer Premier. All the primers were modified by sulfhydryl at the 5' end. The sequences of the primer DNA are:

Primer-1: 5' TGTCAGCGTCATAAGAGGT 3'

Primer-2: 5' CGACCAAACATAAATCACCT 3'

Primer-3: 5' TTGGGAAGTAGCGACAGC 3'

Primer-4: 5' ATTACATCACTCCTTCCGC 3'

Primer-5: 5' AACCTCAGCACTAACCTTG 3'

All oligonucleotides were obtained from Shanghai Sangon biotechnology Co., Ltd. (Shanghai China) and used as obtained. Trisodium citrate, $HAuCl_4$, NaH_2PO_4, Na_2HPO_4, and NaCl were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Tween-20 was obtained from Sunshine biotechnology (Nanjing China) Co., Ltd. Tris-(2-carboxyethyl) phosphine hydrochloride (TCEP) was provided by Thermo Scientific (USA). Double distilled water was used for all of the experiments.

Preparation of Citrate-capped AuNPs. 5 mL of 38.8 mM Tisodium citrate was added rapidly into a stirred boiling aqueous solution containing 50 ml of 1 mM $HAuCl_4$. The solution turned into clear, black, purple and deep red in sequence within 2 min. After the solution was kept boiling and stirred for 15 min, it was naturally cooled down to room temperature. The final colloidal solution was stored at 4 °C for further used. The concentration of AuNPs was 13 nM calculated by lambert-beer law. The extinction coefficient of 2.7×10^8 M^{-1} cm^{-1} at 520 nm for 13 nm AuNPs was used during the calibration.

Preparation of DNA-functionalized AuNPs. To activate the thiol-DNA, 20 μL of 100 μM DNA was added to 5 μL of 20 mM Tris buffer (pH=7.3) containing 100 mM TCEP. The resultant solution was incubated for 1 h at room temperature. After incubation, the activated oligonucleotides were purified using Millipore's Amicon Ultra-0.5 centrifugal filter device to remove excess TCEP. The freshly deprotected and purified DNA was later added to 500 μL of gold colloidal solution to functionalize the AuNPs. The mixed solution was sonicated for 10 s,

and then incubated for 20 min with shaking at room temperature. After that, the resultant solution was mixed with 0.1 M phosphate buffer (pH=7.2) containing 0.1 % sodium dodecyl sulfate (SDS) and the final concentration of phosphate and SDS was 0.01 M and 0.01 %, respectively. The solution was sonicated for 10 s, and incubated for 20 min. In the subsequent salt aging process, the concentration of NaCl first increased to 0.05 M using 2 M NaCl. The process was repeated at one more increment of 0.05 M NaCl and for every 0.1 M NaCl increment thereafter until a concentration of 0.5 M NaCl was reached. After each addition of NaCl, the DNA-AuNPs were votexed, sonicated for 10 s, and then incubated for 20 min. After the salt aging, the mixture was shaken at room temperature overnight. To remove excess DNA, the solution was centrifuged at 13,200 rpm for 20 min, and then redispersed in reaction buffer (pH=8.0) containing 20 mM Tris, 200 mM NaCl, 5 mM $MgCl_2$, and 0.05 % tween-20. Teeen-20 was used to reduce the sticking of AuNPs to eppendorf tube in this work. The step was repeated three times to sufficiently remove excess DNA. The good stability in salt aging process confirmed the successfully coupling of DNA to AuNPs

Preparation of DNA-functionalized AuNRs.

Water-soluble gold nanorods were synthesized via seed-mediated growth routes. First, the seed solution was prepared as follows: 1 mL of CTAB solution (0.2 M) was mixed with 1 mL of $HAuCl_4$ (0.0005 M). While the solution was stirred at 25 °C, 0.12 mL of ice-cold 0.01 M $NaBH_4$ was added, and the resulting seed solution turned to brownish yellow color. Second, the growth solution was synthesized as follows: 50 mL of $HAuCl_4$ (0.001 M), 50 mL of CTAB (0.2 M) and 2.5 mL of $AgNO_3$ (0.004 M) were mixed at 25 °C. After gentle mixing of the solution, 670 μL of ascorbic acid (0.079 M) was added to the solution, and the solution color changed from dark yellow to colorless. To generate nanorods, 120 μL of the seed solution was added to the growth solution at 27-30 °C under gently mixing. Within 10~20 min, the combined solution gradually changed color to brownish red. The solution was then centrifuged to remove the excessive CTAB. The DNA-SH (10 μM, 200 μl) sample was added drop by drop into 400 μl of the gold nanorod solution. The approximate molecular ratio of DNA-SH and gold nanorods was adjusted to be 1.5:1 for the conjugating reaction. The solution was then shaken for 96h at room temperature. Finally, the resulting solution was centrifuged at 13,200 rpm for 20 min and then the supernatant

was decanted to remove unbound DNA-SH.

Preparation of DNA-functionalized PdNPs

Firstly, 0.012 g MUA and 0.1g hydrazine were dissolved into 15 ml of pure water and tune PH of the solution to 12 by 2 M NaOH. Then 5ml of 2 mM Na_2PdCl_4 was gradually added into the above solution under stirring at the temperature 35 °C (the speed of injection is 1 ml/15min), and the solution turned into clear black. Finally the solution was centrifuged at 13,200 rpm for 20 min, and then redispersed in MES buffer. The step was repeated three times to sufficiently remove excess MUA. The concentration of PdNPs is considered as about 1×10^{-9} M and the final colloidal solution was stored at 4 °C for further used.

5 mg EDC and 5 mg NHS were added into 400 μL of above PdNPs solution. The resultant solution was incubated for 30 min with shaking at room temperature. After incubation, the solution was centrifuged to remove supernatant fluid at 4 °C, and then 100μL PBS buffer and 10μL 100 μM NH_2-DNA was added. Finally the resultant solution was incubated for 24 h at room temperature. To remove excess DNA, the solution was centrifuged at 13,200 rpm for 20 min, and then redispersed in Tris buffer (pH=8.0). The step was repeated three times to sufficiently remove excess DNA.

Optimization of PCR process. The 5' end of the primers was modified with a sulfhydryl group (–SH). PCR reactions were performed in 50 μL solution containing 5 μL 10 PCR buffer (50 M KCl, 10 mM Tris-HCl pH 9.0 at 25 °C, 1.5 mM $MgCl_2$), 1 μL dNTPs (1 mM), 7 μL PhiX174 DNA (0.6 μM), and 0.5U of Taq Plus polymerase, 3μL for each primer-AuNPs and H_2O which was added to make the PCR system up to 50 μL. Thermal cycling of PCR was for 5 min at 94 °C pre-denaturation, followed by one cycle of 94 °C denaturation (30 s), Tm 60 °C annealing (30 s), and 72 °C extension (1 min), and then 72 °C (10 min) using PCR machine (Eppendorf Mastercycler). After PCR, the solution was centrifuged at 13,200 rpm for 20 min, the step was repeated three times. All the products were stored at 4 °C. The immobilization of primers and PCR products was analyzed by agarose gel electrophoresis (1.5 %) in 0.5 Tris-borate-EDTA buffer at 90 V for 40 min.