Supporting Information

DNA-Mediated Control of Au Shell Nanostructure and Controlled Intra-Nanogap for Highly Sensitive and Broad Plasmonic Response Range

Haemi Lee[1], Sang Hwan Nam[1], YuJin Jung[1], Jung-Mu Kim[2], Yung Doug Suh[1,3,*] and Dong-Kwon Lim[4,*]

[1]Laboratory for Advanced Molecular Probing (LAMP), Korea Research Institute of Chemical Technology, DaeJeon 305-600, South Korea, [2]Department of Electronic Engineering, Chonbuk National University, 567 Baeckje-daero, Jeonju 561-756, South Korea, [3]School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, South Korea, [4]KU-KIST Graduate School of Converging Science and Technology, Korea University, 145 Anam-ro, Soeongbuk-gu, Seoul 135-467, Korea.

This pdf file includes:

General materials & methods, and supporting figures (Figure S1 – S7).

I. General

The gold nanoparticles were purchased from Ted Pella, Inc. (Redding, CA, USA). All other chemical reagents ($HAuCl_4 \bullet 3H_2O$, poly [N-vinyl-2-pyrrolidone; *Mw*, 40,000; K value, 29–32], $NH_2OH \bullet HCl$, dithiothreitol) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received without further purification. Cy3-modified thiolated single-stranded DNA (ssDNA) was purchased from IDT Inc. (Coralville, IA, USA) and reduced by using dithiothreitol (0.1 M) in a phosphate buffer (0.17 M, pH = 8.0). The reduced oligonucleotides were then purified using NAP-5 column (Sephadex G-25 medium, DNA grade). NANOpure H_2O (>18.0 MΩ) was used for all of the experiments. The formvar/carbon coated copper grid (Ted Pella, Inc.) and high-resolution transmission electron microscopy (JEM-2010, JEOL, Tokyo, Japan) were used for the TEM analysis. For the Raman analysis, we used a homemade Raman microscope equipped with a 532, 660, and 785-nm laser system, placed the particle solution (10 μL of 0.5 nM) on the cover glass, and then obtained the Raman spectra (1.0 sec exposure for a single spectra acquisition with 1.0 mW power at sample).

II. Preparation of the Cy3-ssDNA modified AuNP (seed solution)

A fast salt aging method was used to prepare DNA-modified AuNPs[1]. Freshly reduced thiolated Cy3-modified ssDNA (760 μL of 4.3 μM: 3′-HS-$[CH_2]_3$-[Cy3]-A_{10}-PEG_9-AAACTCTTTGCGCAC-5′) was mixed with citrate-AuNPs (1 mL, 1.0 nM), respectively, and then incubated for 30 min at room temperature. The solution was then adjusted to obtain a final phosphate concentration of 10 mM (pH 7.4) with 100 mM PB (176 μL) and a final concentration of 0.1% (wt/vol) sodium dodecyl sulfate (SDS) with 10% SDS solution (1.9 μL). The solution was further incubated on an orbital shaker for 30 min and the NaCl concentration was increased up to 0.3 M by adding four aliquots of the total volume of the 2 M NaCl solution (0.05 M twice, 0.1 M twice) every 30 min (48.5 μL, 48.5 μL, 97 μL, and 97 μL). Brief (5 min) heating in a water bath (60°C) was applied at every salt addition step to minimize the nonspecific interactions between the Cy3 molecules in the ssDNA and the Au surface. After the salt-aging procedures, the gold and DNA mixture was gently vortexed overnight at room temperature. The solution was centrifuged (12,000 rpm, 15 min), the supernatant was removed, and the precipitate was redispersed in distilled water (DW; twice). The particle concentration was determined by use of a UV-visible spectrophotometer. The

DNA-AuNP in DW was stable for more than six months at room temperature.

III. Preparation of phosphate buffer (pH 5.0, 6.0, 6.5, 7.4, 8.0, and 9.0)

We used a 100 mM phosphate buffer with different pHs to adjust the final buffer concentration of the DNA-AuNP solutions at 10 mM (for example, by adding 10 μL of PB solution to 100 μL of the DNA-AuNP solution dispersed in DW). To prepare **pH 5.0** (100 mM) PB, 13.61 g of $NaHPO_4$-H_2O and 0.36 g of Na_2HPO_4-$7H_2O$ were dissolved in DW (1.0 L). To prepare **pH 6.0** (100 mM) PB, 12.1 g of $NaHPO_4$-H_2O and 3.2 g of Na_2HPO_4-$7H_2O$ were dissolved in DW (1.0 L). To prepare **pH 6.5** (100 mM) PB, 9.6 g of $NaHPO_4$-H_2O and 8.0 g of Na_2HPO_4-$7H_2O$ were dissolved in DW (1.0 L). To prepare **pH 7.4** (100 mM) PB, 5.8 g of $NaHPO_4$-H_2O and 15.4 g of Na_2HPO_4-$7H_2O$ were dissolved in DW (1.0 L). To prepare **pH 8.0** (100 mM) PB, 0.94 g of $NaHPO_4$-H_2O and 24.9 g of Na_2HPO_4-$7H_2O$ were dissolved in DW (1.0 L). To prepare **pH 9.0** (100 mM) PB, 0.1 g of $NaHPO_4$-H_2O and 26.6 g of Na_2HPO_4-$7H_2O$ were dissolved in DW (1.0 L).

IV. FEM-lab based simulations

We performed FEM-lab based simulations using software (Ansoft HFSS™, Ansys Inc., USA). A linearly (x) polarized plane wave (λ = 660, 785-nm) is incident on the half-shell, complete-shell (1.2 nm, 2.1 nm intra-nanogap), and star shape with an irregular nanogap. The environmental material outside of each shell was set to water in order to have a similar condition to the Raman experiments. We used the empirical dielectric constants of gold reported by Rakic[2] and Johnson and Christy[3] with interpolation. The relative permeability of gold is assumed to be μ_r =1, with a dielectric constant of $\varepsilon_{Au}(\lambda) = n^2\text{-}k^2$. The dielectric constants of the mixture of air and DNA, the mixture of water and DNA in the gap, and the water are $\varepsilon_{air + DNA}$ = 1.002, $\varepsilon_{water + DNA}$ = 1.767541, and ε_{water} = 1.7689 (obtained by adopting the Maxwell-Garnett formalism).

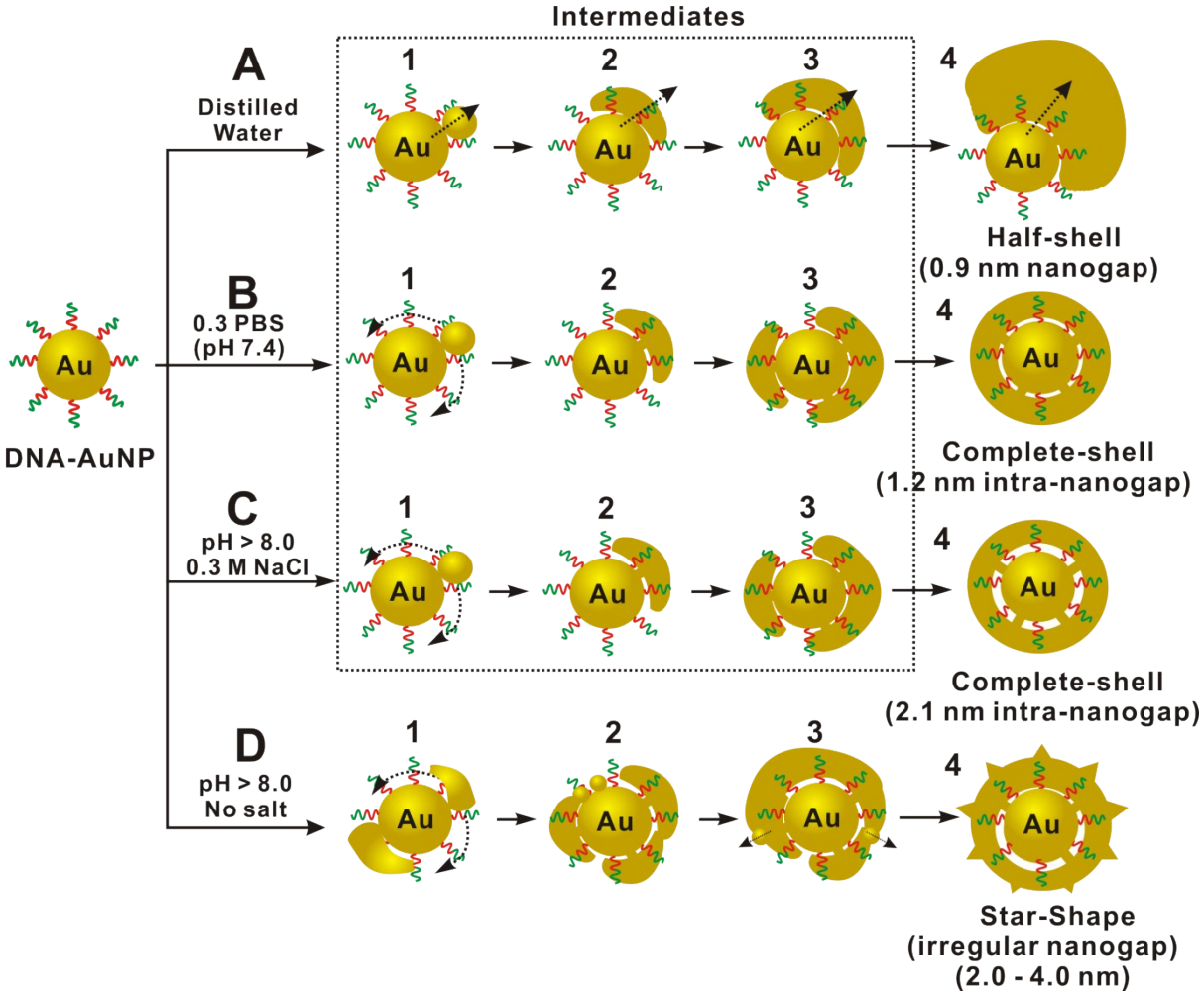

Figure S1. Schematic descriptions of the intermediates and final structures. (**A**) half-shell structure with narrow nanogap (0.9 nm) was obtained from distilled water (DW) conditions, (**B**) complete-shell with uniform intra-nanogap (1.2 nm) was obtained from seed solution (0.3 M phosphate buffered saline), (**C**) complete-shell with wide intra-nanogap (2.1 nm) was obtained from weak basic conditions in the presence of NaCl (pH 8.0) and (**D**) the star-shaped particle with irregular intra-nanogap (2.0 – 4.0 nm) was obtained from the weak basic condition without sodium chloride.

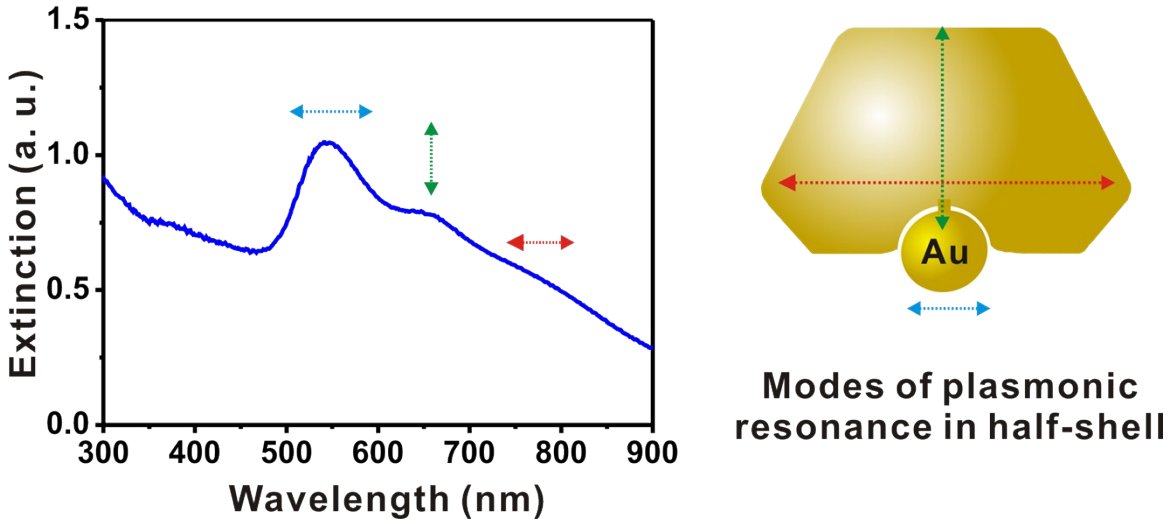

Figure S2. UV-Vis spectra and possible mode of plasmonic resonance of half-shell (representative LSPR modes are displayed with blue, green, and red arrows).

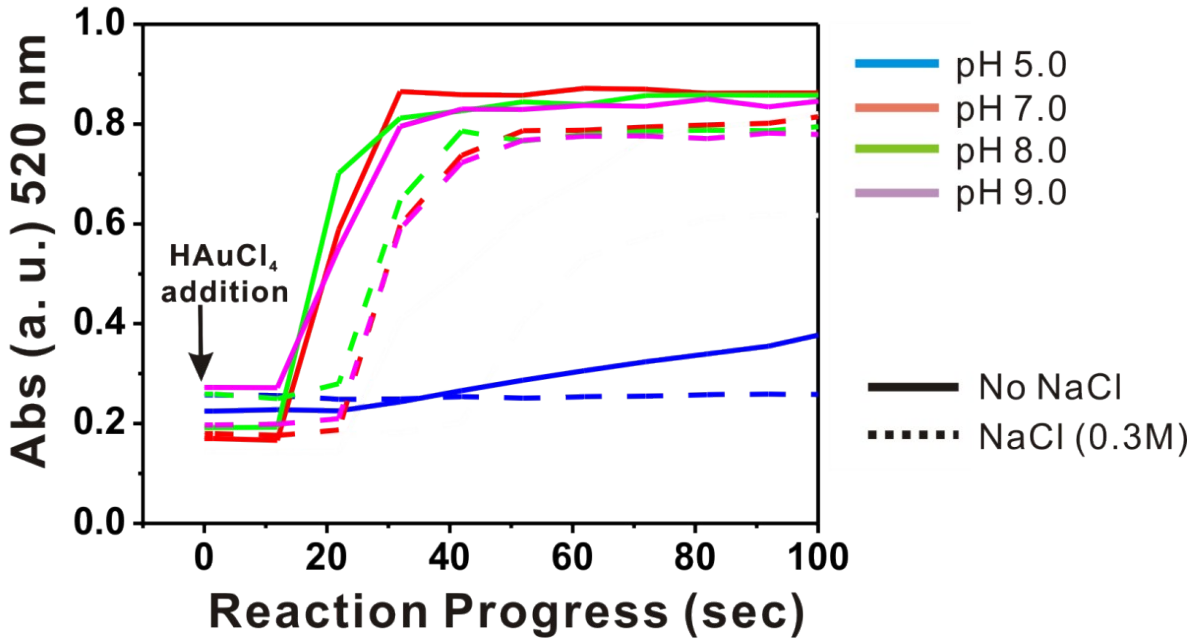

Figure S3. The effect of NaCl for the reaction progress of Au-shell formation reactions (the addition of NaCl induced slow reaction progress regardless of the seed solution pH [5.0, 7.0, 8.0, and 9.0]).

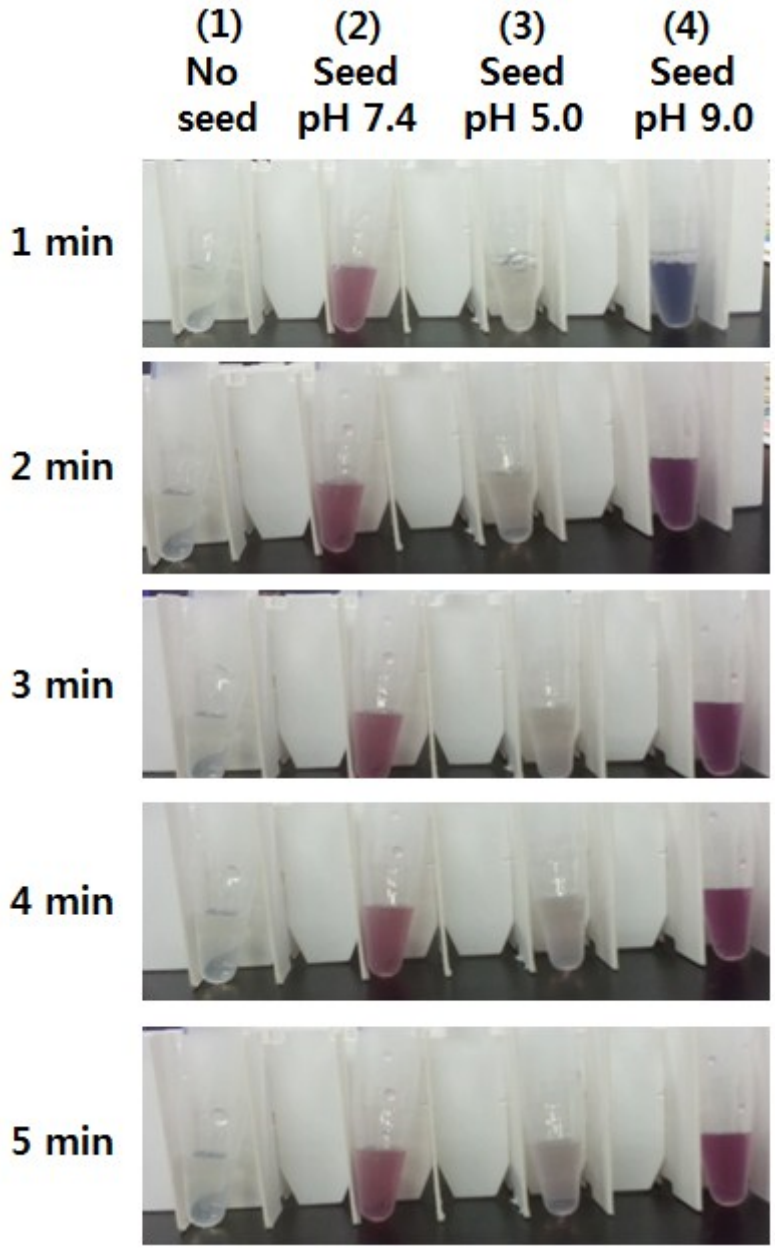

Figure S4. The time-dependent solution color changes of Au shell formation reactions without seed (1), with DNA-AuNPs seed and pH 7.4 condition (2), pH 5.0 condition (3), pH 9.0 condition (4).

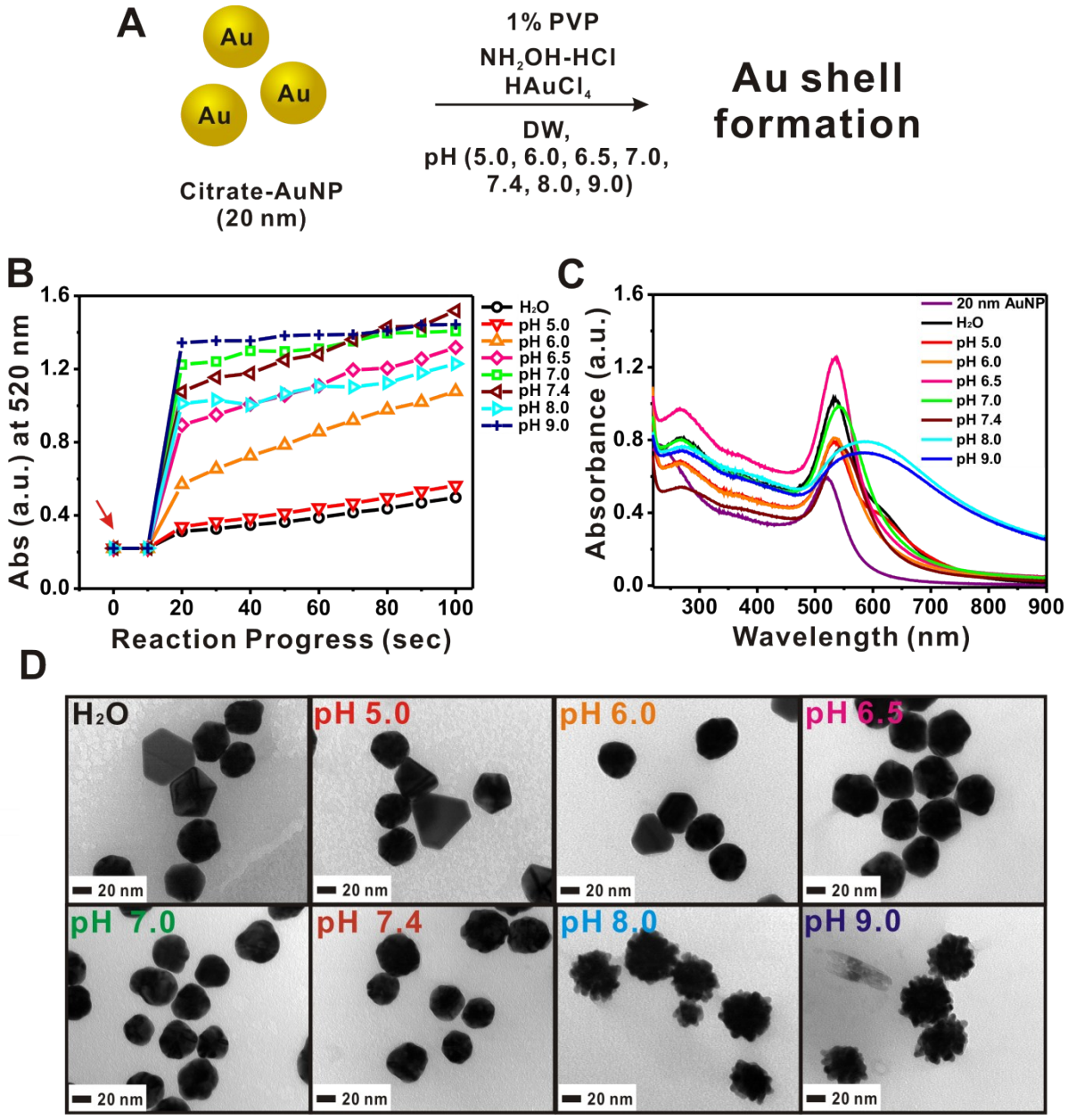

Figure S5. (A) Schematic descriptions of reactions with citrate-AuNP (20 nm), (B) the reaction progress in different pHs, (C) UV-Vis spectra of products, and (D) TEM images of products obtained from DW and various pH (5.0, 6.0, 6.5, 7.0, 7.4, 8.0, and 9.0) conditions.

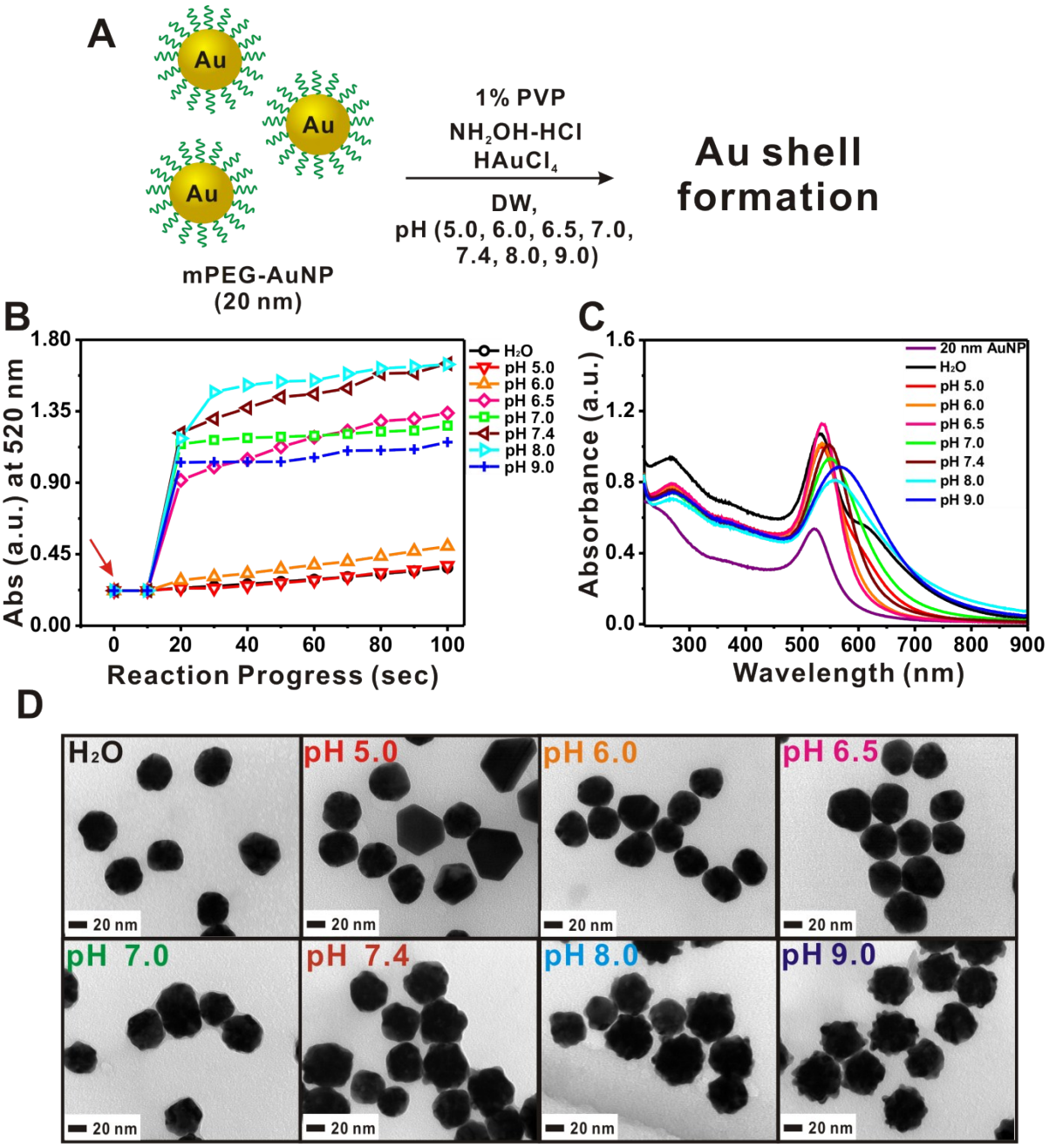

Figure S6. (A) Schematic descriptions of reactions with mPEG-AuNP (20 nm), (B) the reaction progress in different pHs, (C) UV-Vis spectra of products, and (D) TEM images of products obtained from DW and various pH (5.0, 6.0, 6.5, 7.0, 7.4, 8.0, and 9.0) conditions.

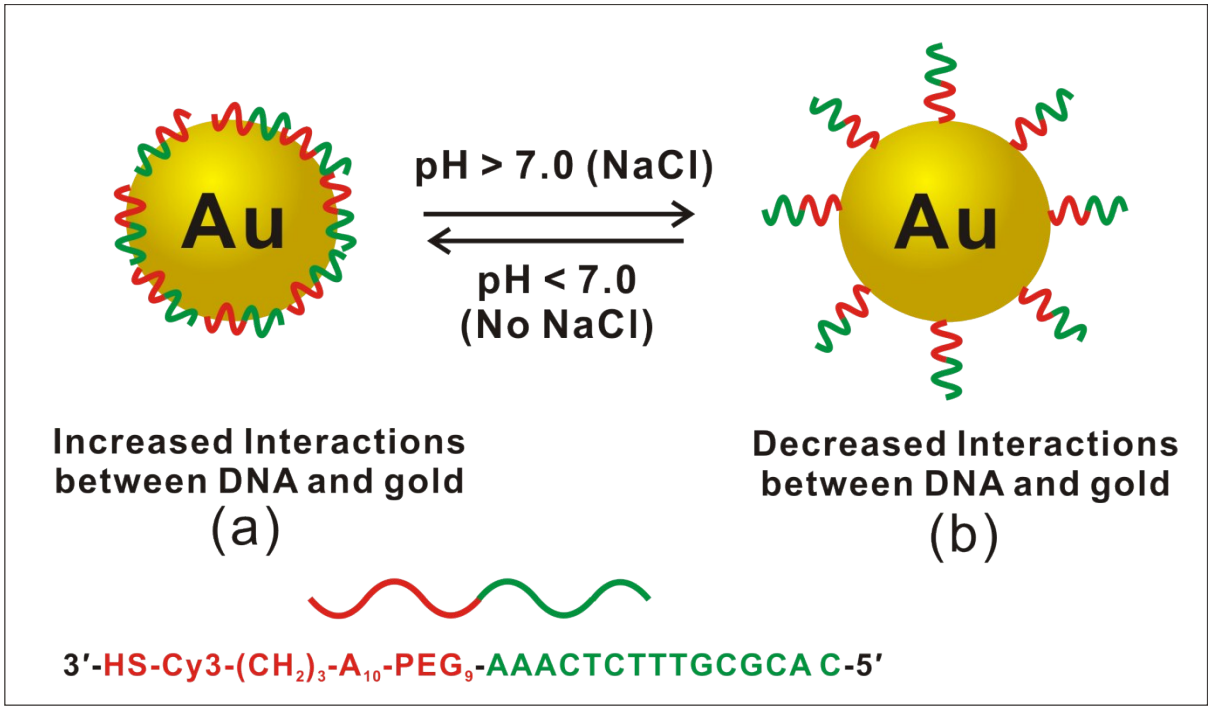

Figure S7. The description of DNA interactions on gold surface depends on pH and salt concentrations. Low pH (<7.0) conditions and low NaCl concentrations induce the increased interactions of the DNA base to the gold surface due to the protonation of phosphate backbone (a). In contrast, high pH conditions with NaCl can induce decreased interactions of the DNA base and gold, which can lead to the proposed structure (b).[4]

References

1. Hurst, S. J.; Lytton-Jean, A. K. R.; Mirkin, C. A. *Anal. Chem.* **2006,** 78, 8313-8318.

2. Rakic, A. D. et al.,. *Appl. Opt.* **1998,** 37, (22), 5271-5283.

3. P. B. Johnson and R. W. Christy. Optical Constants of the Noble Metals, *Phys. Rev. B,* **1972**, 6, 4370-4379.

4. Chen, C.; Song, G.; Ren, J.; Qu, X. *Chemical Communications* **2008**, (46), 6149-6151.