Supplementary Information for

Nanoplasmonic Detection of Adenosine Triphosphate by the Aptamer Regulated Self-Catalytic Growth of Single Gold Nanoparticle

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1. Experimental

Materials

Anti-ATP aptamer (5'-ACCTGGGGGAGTATTGCGGAGGAAGGT-3') was synthesized by TaKaRa Biotechnology Co. (Dalian, China) and purified by HPLC. ATP, CTP, GTP, UTP, 3-mercaptopropyl trimethoxysilane (95% v/v) and $HAuCl_4 \cdot 3H_2O$ (>99.0%) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. Sodium citrate and other chemicals were of analytical grade, and all chemicals were used without further purification. All solutions were prepared with Milli-Q water (18 MΩ·cm) from a Milli-Q System (Millipore, USA).

Preparation of GNPs

GNPs with an average diameter of ~60 nm were synthesized according to the citrate reduction method. In brief, 50 mL of $HAuCl_4$ (0.01% wt%) was brought to boil in an oil bath under vigorous stirring. Then 230 μL of sodium citrate (1% wt%) was rapidly injected into the boiling solution, which results a significant color change from yellow to black and finally to purple. After another 10 min of boiling, the resulting mixture was allowed to cool down to room temperature under stirring, and then filtered through a 0.8 μm membrane. The optical absorbance of the resulting GNPs was characterized by USB 2000+ UV-vis spectroscopy (Ocean Optics, USA). The characteristic SPR absorption peak centered at 535 nm was observed.

Modification of glass slides with GNP

The GNPs were modified on silanized microscopy glass slides. Before modification, the microscopy slides were first cleaned by thoroughly rinsing with methanol, blow-dried with N_2, then treated with UV ozone cleaner for 25 min for each side. The cleaned slides were checked with water contact-angle measurements. Slides with a contact angle less than 10° were considered as sufficiently clean and used for further modification. Then the cleaned slide was immersed into an ethanol solution of 1% (v/v) 3-mercaptopropyl trimethoxysilane for 1 h, followed by successive rinsing with ethanol, blow-drying with N_2 and heating at 110 ^{o}C in an oven for 30 min. The silanized microscopy slides were modified with diluted GNPs solution (0.05 nM) for 5 min. The GNPs functionalized slides were rinsed with water to remove physically adsorbed GNPs and dried with N_2 for further DFM measurements.

Single nanoparticle DFM imaging and scattering spectroscopy measurements

The dark-field measurements were carried out on an inverted microscope (eclipse Ti-U, Nikon, Japan) equipped with a dark-field condenser (0.8 <NA<0.95) and a 40× objective lens (NA=0.8). The GNPs functionalized microscopy slides were

immobilized on a platform, and a white light source (100 W halogen lamp) was used to excite GNPs and generate plasmon resonance scattering light. The scattered light was collected by a true-color digital camera (Nikon DS-fi, Japan) to generate the dark-field color images, and was also splitted by a monochromator (Acton SP2300i, PI, USA) that was equipped with a grating (grating density: 300 lines/mm; blazed wavelength: 500 nm) and recorded by a spectrograph CCD (CASCADE 512B, Roper Scientific, PI, USA) to generate the scattering spectra. The scattering spectra from individual nanoparticle were corrected by subtracting the background spectra taken from the adjacent regions without GNPs and dividing with the calibrated response curve of the entire optical system.

ATP-induced self-catalytic growth of single GNP

The aptamer-GNPs were prepared by non-covalently attachment of anti-ATP aptamer on GNPs. Briefly, 100 μL of anti-ATP aptamer (10 μM) in a buffer solution containing 10 mM of Tris-HCl (pH 7.2) and 100 mM of NaCl was dropcasted on the GNPs modified slides and then incubated for 10 min. After that, the obtained slides were successively rinsed with a buffer solution containing 10 mM of Tris-HCl to remove the loosely adsorbed aptamers. Then 100 μL of ATP of different concentrations was dropcasted on the resulting slides. After another 30 min of incubation, the slides were washed with 10 mM of Tris-HCl buffer solution (pH 7.2) and dried with N_2.

The self-catalytic growth of GNPs was carried out by dropcasting a growth solution (100μL) containing glucose (30 mM), $HAuCl_4$ (0.5 mM) and Tris-HCl (10 mM, pH 7.2) on the resulting slides. The self-catalytic growth of GNPs was real-time monitored by DFM and the PRRS spectra of the growing GNPs were continuously recorded with a time interval of 5 min. All the measurements were taken under room temperature (25±1°C).

2. Figures

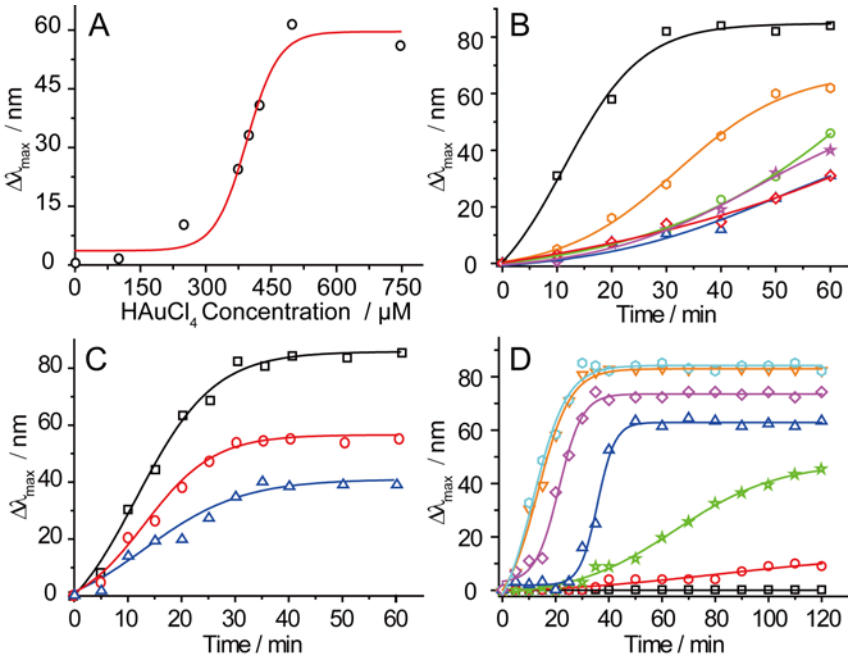

Fig. S1. (A) The λ_{max} changes ($\Delta\lambda_{max}$) of 60 nm GNPs after 30 min of self-catalytic growth in the presence of 50 mM of glucose at different concentrations of $HAuCl_4$. (B) Time-dependent $\Delta\lambda_{max}$ of 60 nm corresponding to different concentrations of aptamers in the presence of 0.5 mM of $HAuCl_4$ and 30 mM of glucose. (□) 0 μM, (▽) 1 μM, (○) 10 μM, (☆) 20 μM, (△) 30μM, (◇) 60 μM. (C) Time-dependent $\Delta\lambda_{max}$ corresponding to three selected GNPs of 60 nm (□, with initial λ_{max} located at 560 nm), 80 nm (○, with initial λ_{max} located at 590 nm) and 110 nm (△, with initial λ_{max} located at 630 nm) in the presence of 0.5 mM of $HAuCl_4$ and 30 mM of glucose. (D) Time-dependent $\Delta\lambda_{max}$ changes of 60 nm GNPs in the self-catalytic growth corresponding to different concentrations of glucose. (□) 0 mM, (○) 5 mM, (☆) 7.5 mM, (△) 10 mM, (◇) 20 mM, (▽) 30 mM, (⬡) 40 mM.

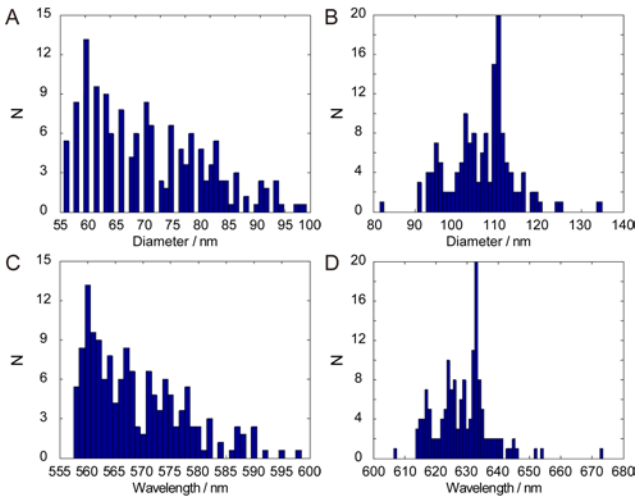

Fig. S2. Diameter distribution of 150 aptamer-GNPs upon incubation with ATP before (A) and after (B) self-catalytic growth by SEM characterization. (C) and (D) are the experimentally analyzed wavelength distribution corresponding to (A) and (B).

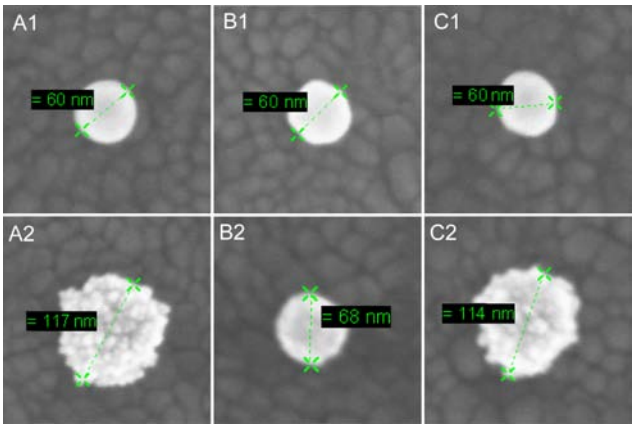

Fig. S3. SEM images of bare GNP (A), aptamer-GNP (B) and aptamer-GNP upon incubation with ATP (C) before (A1, B1, C1) and after (A2, B2, C2) self-catalytic growth.

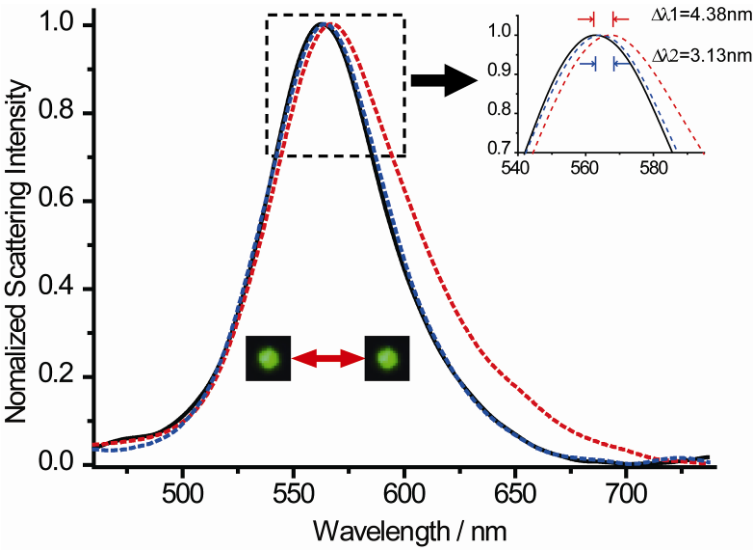

Fig. S4. The PRRS spectra of the representative bare GNP (black curve), aptamer-GNP (red curve) and aptamer-GNP upon incubation with ATP (blue curve). The inset shows the partial enlarged drawing of PRRS spectra.