Electronic Supplementary Information

A pH-responsive DNA nanomachine-controlled catalytic assembly of gold nanoparticles

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S1 Experimental Section

S1.1 Materials

The DNA sequences used in this study (Table S1) were synthesized by Sangon Biotech Co., Ltd. (Shanghai, China). The triplex-forming strand (linker) was adapted from previous work reported by Ricci *et al*.[1] Tris (2-carboxyethyl) phosphine hydrochloride was purchased from Alfa Aesar. Other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Ultrapure water (18.2 MΩ·cm) (Millipore Co., USA) was used in all experiments.

S1.2 Procedure for Synthesis of Gold Nanoparticles (AuNPs)

The 13 nm AuNPs were prepared according to the method proposed by Mirkin.[2] First, sodium citrate solution (10 mL, 38.8 mM) was added to the refluxing $HAuCl_4$ solution (100 mL, 1 mM) quickly. Then, the reaction was allowed to proceed for 10 min under boiling state, the solution color changed from pale yellow to wine red during this time. The next step was to keep stirring for 15 min without heat. Lastly, the solution was filtered through a 0.45 μm nylon filter. The obtained AuNPs surface plasmon resonance maximum (λ_{max}) was 520 nm. AuNPs concentration was measured using UV-vis spectrophotometer (molar extinction coefficient was 2.7×10^8 M^{-1} cm^{-1} at $\lambda_{520\,nm}$ for 13 nm AuNPs[3]).

S1.3 Preparation of DNA-Functionalized AuNPs

AuNPs functionalized with thiol-modified DNA were prepared according to the literature of Mirkin *et al*.[3] AuNPs was mixed with thiolated DNA (treated with TCEP beforehand) in a 1:350 molar ratio for 16 h at first. Subsequently, phosphate buffer (PB) was added to the mixture to attain a concentration of 10 mM for 12 h. Then, the mixture was sequentially aged in 0.1, 0.2 and 0.3 M NaCl, each step lasted 8 h. Finally, the solution was centrifuged three times (15000 rpm, 30 min), and the obtained oily precipitate was dissolved in 0.1 M phosphate buffered saline (10 mM PB, 0.1 M NaCl, pH = 7.4) then stored at 4 °C for further use.

S1.4 DNA Oligonucleotides Handling and Preparation of Substrate

All DNA oligonucleotides were dissolved in 0.1 M phosphate buffered saline (10 mM PB, 0.1 M NaCl, pH = 7.4), and their concentrations were measured using a UV–vis spectrometer. The linker and protector strands were mixed in molar ratio of 1:1, maintained at 90 °C for 15 min, and cooled to room temperature gradually. All DNA samples were stored at 4 °C for further use.

S1.5 Experimental Condition

All experiments were operated at 25 °C, and the pH values of the reaction buffer (10 mM PB, 0.1 M NaCl) in specific experiment were adjusted with the addition of HCl or NaOH. The kinetics process of DNA–AuNP assembly was measured using an Agilent Cary 300 UV-vis spectrometer (Santa Clara, CA, USA) as follows. First, the samples were prepared by adding substrate into the mixture of AuNP-1 and AuNP-2 in the plastic tubes. Second, trigger was added, and all samples were transferred to the microcells of the UV–vis spectrometer. Finally, the aggregation process of the pH-responsive DNA–AuNP assembly was monitored through tracking the absorption value of the DNA–AuNP sample at λ_{max} = 520 nm every 5 min.

S2 Supplementary Figure

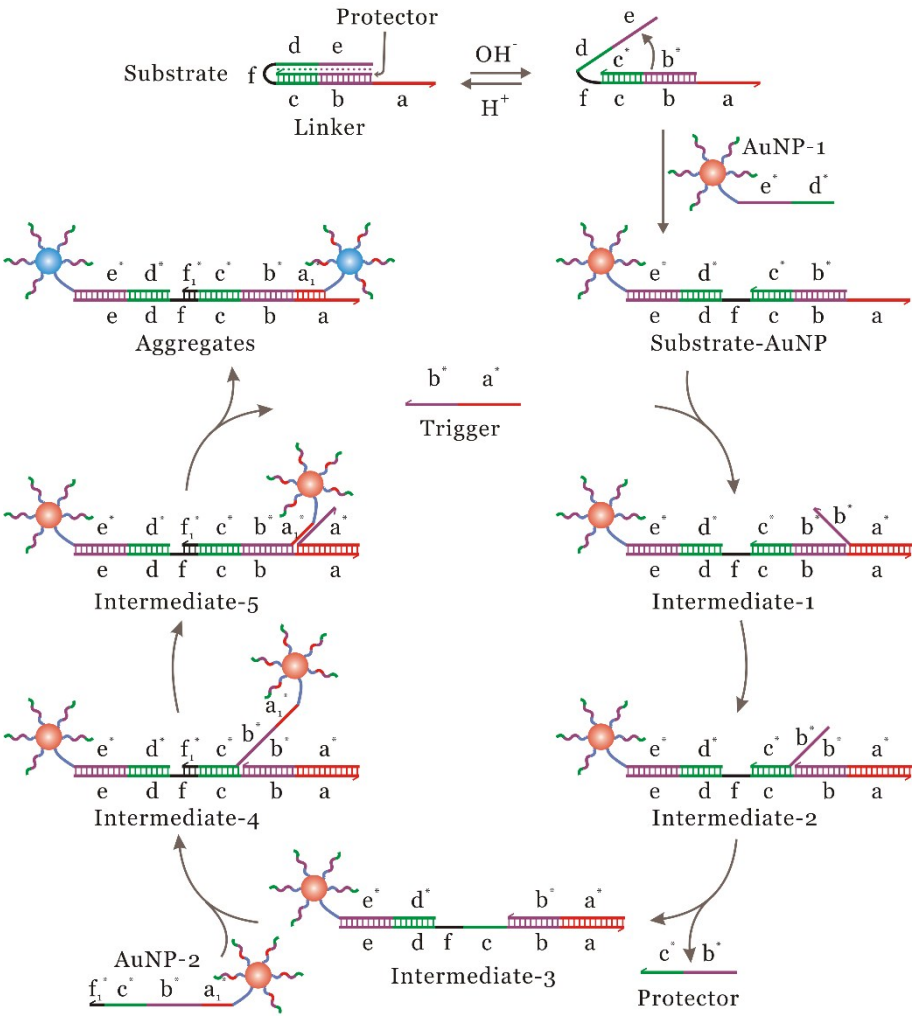

Fig. S1 Graphical representation of the catalytic assembly of DNA−AuNPs driven by a pH-responsive DNA nanomachine in detail.

S3 Sequences of DNA Oligonucleotides

Name	Sequences (5' to 3')
Linker	TTCCTTTCTCCTTCTTTTAACTATTTTCTTCCTCTTTCCTTCTTACAT TCCAC
Linker-1 mismatch	ATCCTTTCTCCTTCTTTTAACTATTTTCTTCCTCTTTCCTTCTTACA TTCCAC
Linker-2 mismatches	AACCTTTCTCCTTCTTTTAACTATTTTCTTCCTCTTTCCTTCTTACA TTCCAC
Linker-3 mismatches	AAACTTTCTCCTTCTTTTAACTATTTTCTTCCTCTTTCCTTCTTACA TTCCAC
Linker-4 mismatches	AAATTTTCTCCTTCTTTTAACTATTTTCTTCCTCTTTCCTTCTTACA TTCCAC
Protector	AAGGAAAGAGGAAGAAAA
Trigger	GTGGAATGTAAGAAGGAAAGAG
AuNP-1	AAAAGAAGGAGAAAGGAATTTTTTTTTTTTTTT-SH
AuNP-2	SH-TTTTTTTTTTGTAAGAAGGAAAGAGGAAGAAAATAG

Table S1 The DNA oligonucleotides sequences used in this study.

References

1. A. Amodio, B. Zhao, A. Porchetta, A. Idili, M. Castronovo, C. Fan and F. Ricci, *J. Am. Chem. Soc.*, 2014, **136**, 16469-16472.
2. J. J. Storhoff, R. Elghanian, R. C. Mucic, C. A. Mirkin and R. L. Letsinger, *J. Am. Chem. Soc.*, 1998, **120**, 1959-1964.
3. R. Jin, G. Wu, Z. Li, C. A. Mirkin and G. C. Schatz, *J. Am. Chem. Soc.*, 2003, **125**, 1643-1654.