Supporting Information

DNA-Templated Ag Nanoclusters as Signal Transducer for Label-free and Resettable Keypad Lock

Zhixue Zhou, Yaqing Liu and Shaojun Dong*

Experimental Section

Materials

Oligonucleotides with specific sequences were synthesized by Shanghai Sangon Biotechnology Co. Ltd. (Shanghai, China). The concentrations of oligonucleotides were determined using the 260 nm UV absorbance with the corresponding extinction coefficient. Exonuclease III (1.5×10^5 U/mL) was purchased from TaKaRa Biotechnology Co. Ltd (Dalian, China). Other reagents were of analytical grade and used as received. All aqueous solutions were prepared with ultrapure water (＞18 MΩ) from a Milli-Q Plus system (Millipore).

Characterization

The fluorescence emission spectra of Ag nanoclusters (Ag NCs) were collected from 530 to 750 nm using a Fluoromax-4 Spectrofluorometer (HORIBA Jobin Yvon, Inc., NJ, USA) at room temperature. The excitation wavelength was set at 517 nm. The fluorescence excitation spectrum of Ag NCs was collected from 400 to 550 nm with the emission wavelength at 568 nm.

UV-vis absorption spectra were recorded by a CARY 500 UV/vis-near-IR Varian spectrophotometer. The melting curves were obtained from the absorption at 260 nm versus temperature. The interval temperature is 1°C and the ramp rate is 1°C /min.

Synthesis of Ag NCs with Different DNA Templates

In a typical synthesis experiment, $AgNO_3$ (6 μM) was added into the DNA templates (1 μM) dissolved in PBS buffer (20 mM phosphate, pH 7.4, 1 mM magnesium acetate). After the mixtures were stirred for 30 s, they were reduced with $NaBH_4$ (6 μM) for 0.5h.

Ag NCs as Transducer for Molecular Keypad Lock

Six copies of C-DNA in PBS buffer are prepared as the initial systems, and then the combinational inputs with various sequences were respectively added into the solutions. Next, $AgNO_3$ was added and incubated for 5 min. After the solutions were reduced with $NaBH_4$ for 0.5h, they were used for fluorescent measurements. The concentration of each DNA strands is 1 μM, and the total volume of the reaction solution is 400 μL. The incubation time for the first input is 1 h, and 15 min for the second and third inputs.

The system could be reset by means of nuclease-catalyzed DNA hydrolysis reaction. Exonuclease III (Exo III, 20 U mL^{-1}) was added into the systems and incubated for 30 min. Then, the solutions were heated at 80°C for 5 min, followed with a slow annealing treatment. The final systems could be available for the next input signals.

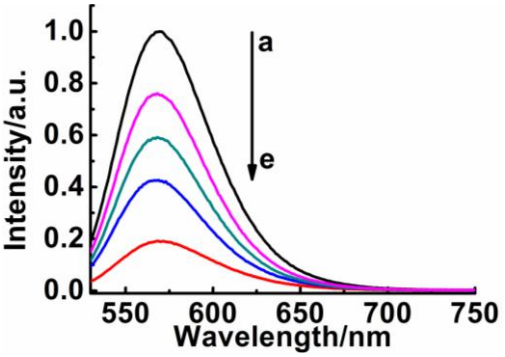

Fig. S1 Fluorescent spectra of Ag NCs stabilized by different DNA templates: (a) B/C-DNA, (b) B/C-DNA + 0.25 μM G-DNA, (c) B/C-DNA + 0.5 μM G-DNA, (d) B/C-DNA + 0.75 μM G-DNA, (e) B/C-DNA + 1 μM G-DNA. G-DNA was added before the synthesis of Ag NCs.

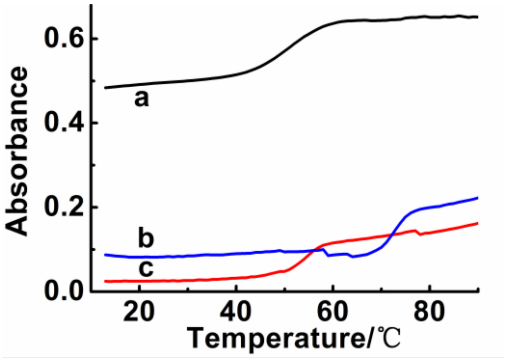

Fig. S2 Thermal denaturation curves for (a) A/C-DNA, (b) G/C-DNA and (c) B/C-DNA at 260 nm. The melting temperatures (T_m) are 51°C for A/C-DNA, 73°C for G/C-DNA, and 55°C for B/C-DNA, respectively.

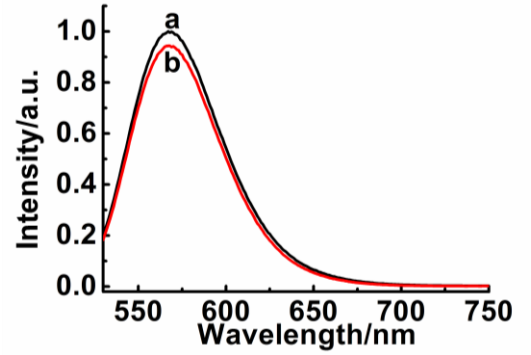

Fig. S3 Fluorescent spectra of solutions containing Ag NCs: (a) B/C-DNA as template; (b) addition of G-DNA into solutions of B/C-DNA-templated Ag NCs.

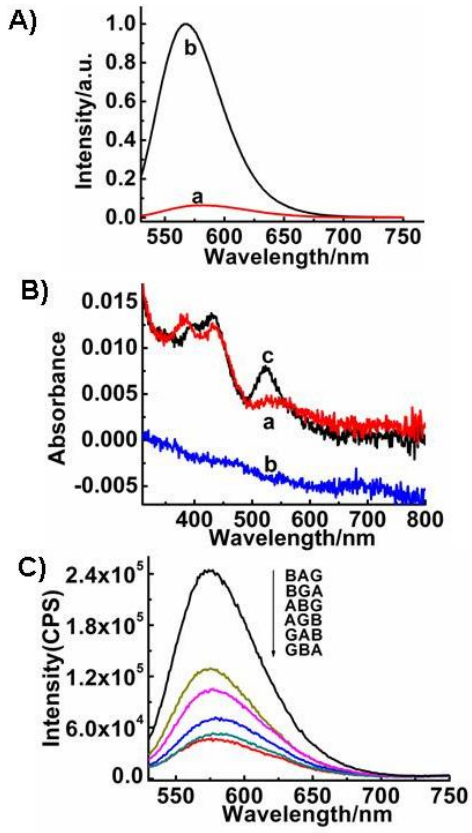

Fig. S4 A) Fluorescent spectra of the systems (a) triggered by the correct input sequence BAG, (b) addition of 20 U mL^{-1} Exo III into (a). B) UV-vis spectra of (a) the system triggered by input BAG and reaction with 20 U mL^{-1} Exo III; (b) Ag^{+} (6μM); (c) the system triggered by input BAG. C) Fluorescent spectra of the systems with corresponding input sequences after reaction with 20 U mL^{-1} Exo III.

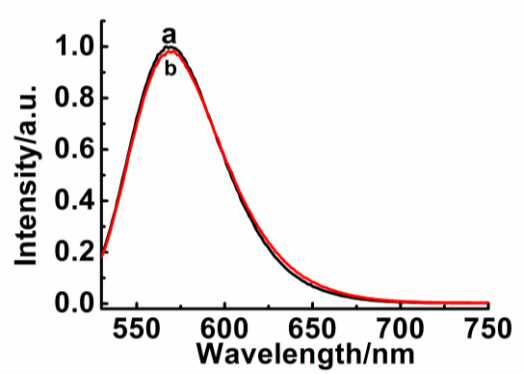

Fig. S5 (a) Fluorescent spectra of the ON state triggered by the correct input sequence BAG; (b) Fluorescent spectra of the ON state after reaction with 20 U mL^{-1} heat-treated Exo III.