SUPPORTING INFORMATION

DNA-based Logic Gates Operating as Biomolecular Security Device

EXPERIMENTAL SECTION

Materials and methods

Tetraethylorthosilicate (TEOS), 3-(aminopropyl)trimethoxysilane (APTS), and BSA were purchased from Sigma-Aldrich (St. Louis, MO, USA). Glutaraldehyde (50% v/v) was purchased from Alfa (Ward Hill, MA). All oligonucleotides were purchased from Sangon Biotechnology Inc. (Shanghai, China) and used without further purification. The sequences used are as follows:

A 5'-GTGTT TATAG CGGAC CCC-$(CH_2)_6$-NH_2-3'

B 5'-GGGGT CCGCT ATAAA CACCT CCAAG AGTGA TATGC CAC-3'

C 5'-CACAT TACGA GTCTT CGTGG CATAT CACTC TTGGA G -3'

D 5'-GAAGA CTCGT AATGT GAAAC CG-3'

DNA was prepared in buffer (20 mM Tri-HCl, 100 mM NaCl, 5 mM $MgCl_2$, pH 8.0). The DNA concentration was determined by measuring the absorbance at 260 nm at high temperature (90℃) by using a JASCOV-550 spectrophotometer, equipped with a temperature-controlled cuvette holder controlled by using a circulating bath. Genefinder was purchased from Bio-v Company (Xiamen, China). The water was purified using a Millipore filtration system. Fluorescence spectra were obtained with a JASCO FP6500 spectrophotometer (Jasco InternationalCo., Ltd., Tokyo, Japan). The excitation wavelength was 490 nm. SEM images were obtained with a Hitachi S-4800 FE-SEM.

Synthesis and modification of silica nanoparticles

The SiNPs were synthesized through hydrolysis of tetraethoxysilane (TEOS) in a mixture of ethanol and water in the presence of ammonia. TEOS dissolved in ethanol was added dropwise into a mixture of water, ethanol, and NH_4OH with vigorous

stirring. After surface modification with (3-aminopropyl)trimethoxysilane (APTS), 5% glutaraldehyde solution in SSC buffer (15 mM sodium citrate, 150 mM NaCl, pH 7.4) was added and the suspension was incubated for 3 hours at room temperature. The material was subsequently washed with SSC buffer to remove excess glutaraldehyde. The solution of 3'-amine-modified DNA was added and the mixture was incubated overnight with shaking. The nanoparticles were then washed with SSC buffer and placed in 0.03% (w/v) $NaBH_3CN$ solution for 30 min. The material was then washed with SSC buffer. Followed by addition of BSA (1 mg/mL in 13× SSC buffer), and stirred for 30 min. The mixture was centrifuged, and rinsed with 13× SSC buffer. The final deposition was suspended in SSC buffer and stored at 4℃ for further use.

DNA assembly on blocked SiNPs and detection

Various combinations of DNA were added to the SiNPs in SSC buffer (15 mM sodium citrate, 150 mM NaCl, pH 7.4, 1000 μL). The resulting mixtures were incubated for 30 min at room temperature. Free DNA was removed via centrifuging, washing, and redispersing steps after each hybridization reaction. The final mixtures were dispersed in 400 μL of buffer for fluorescence measurements. Genefinder (0.5×) was added, and the fluorescence spectra were measured with the excitation wavelength of 490 nm.

Polyacrylamide gel electrophoresis

The DNA ensembles were formed by combined the equimolar quantities in 5 μL of SSC buffer. The electrophoresis was run through 20% polyacrylamide gel in 1×TBE (89 mM Tris base, 89 mM Boric acid, 2 mM EDTA, pH 8.0) on a BioRad electrophoresis unit (Fisher Biotech) at 4□ (100 V, constant voltage) for 1.5 h. The gel was silver-stained. The image was obtained with GDS8000 UV transilluminator.

Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX)

SEM images of SiNPs were obtained with a Hitachi S-4800 FE-SEM. Samples were prepared by pipetting 2 μL of colloid solution onto a silicon wafer with suitable size.

After evaporating the solvent, the silicon wafer was dried overnight under vacuum. The samples were coated with a thin layer of gold before examination in the microscope. SEM was applied to determine the morphology under an accelerating voltage of 10.0 kV. EDX analysis was conducted by means of SEM to identify the chemical composition. 10 μL of colloid solution was deposited on conductive adhesive and dried overnight under vacuum. An accelerating voltage of 20.0 kV was applied.

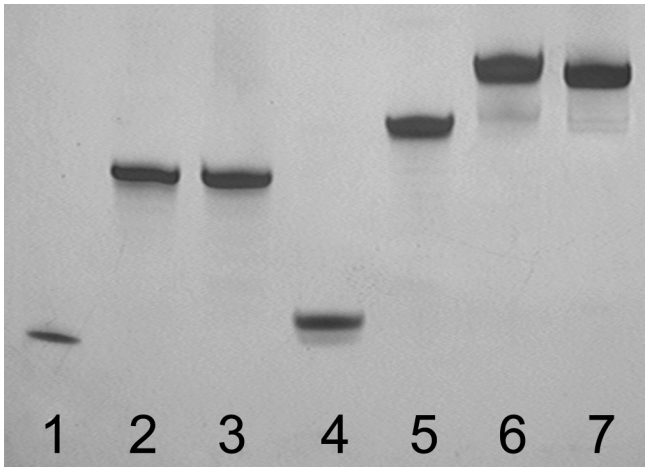


Figure S1. Gel electrophoresis analysis of DNA. Lane1. strand A; Lane2. strand B; Lane3. strand C; Lane4. strand D; Lane5 strand A+B; Lane6. strand A+B+C; Lane7. strand A+B+C+D.

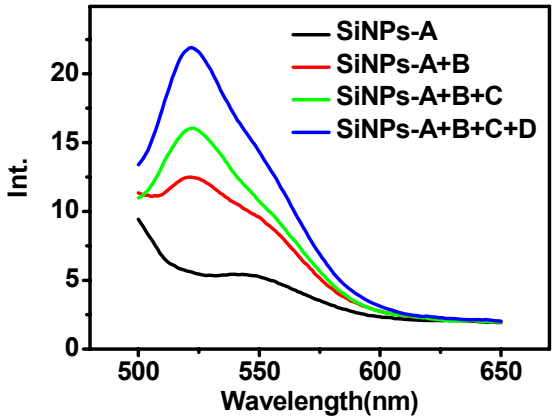


Figure S2. Fluorescence spectra of Genefinder in the presence of different DNA inputs. The excitation wavelength was 490 nm.

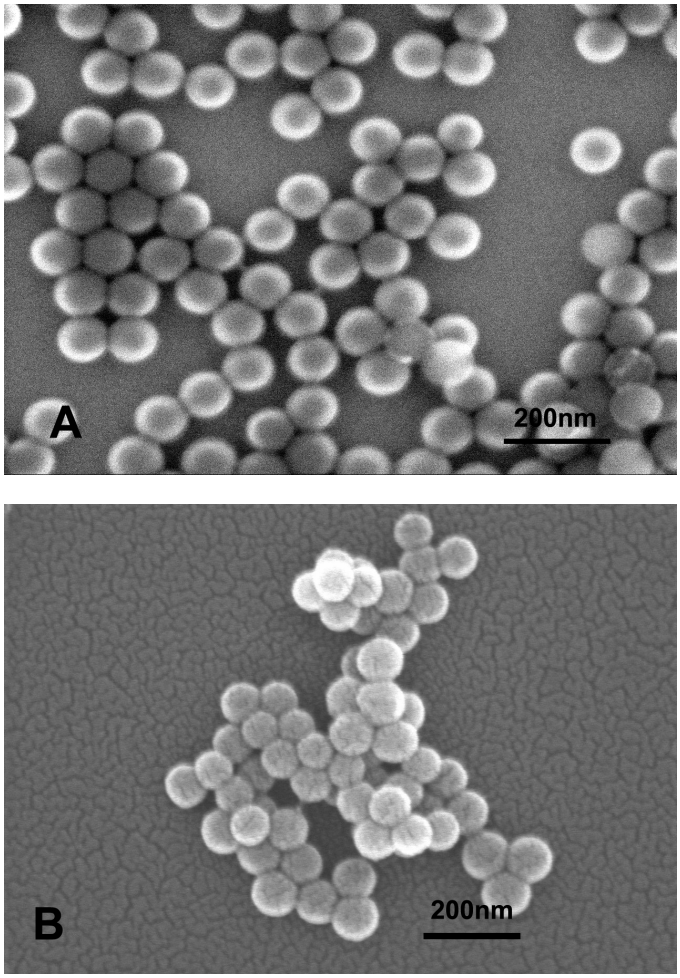
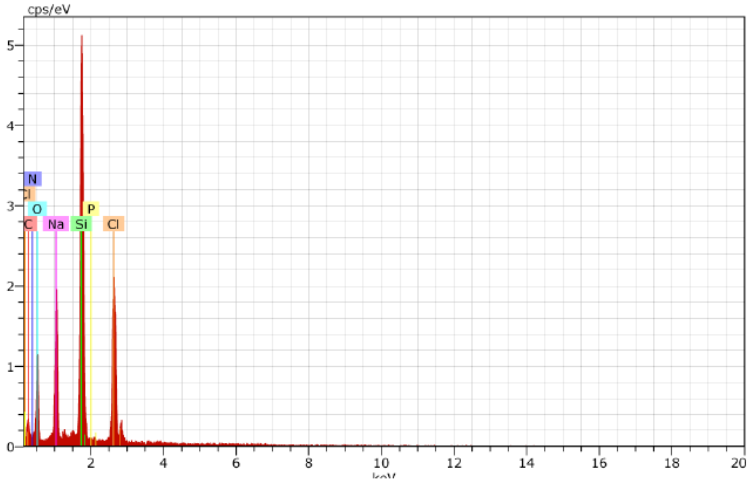


Figure S3. Scanning electron microscope (SEM) images of silica nanoparticles (A) before and (B) after DNA immobilization.



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
C	6	K-series	6.58	7.28	11.52	2.4
N	7	K-series	10.81	11.96	16.23	3.6
O	8	K-series	33.05	36.57	43.42	5.9
Na	11	K-series	7.74	8.57	7.08	0.6
Si	14	K-series	17.00	18.80	12.72	0.8
P	15	K-series	0.28	0.31	0.19	0.1
Cl	17	K-series	14.92	16.50	8.84	0.6
		Total:	90.38	100.00	100.00	

Figure S4. Energy-dispersive X-ray spectroscopy (EDX) of silica nanoparticles after DNA immobilization.

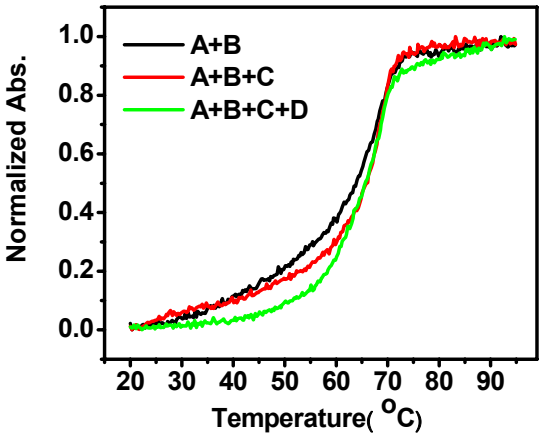


Figure S5. The melting profile of DNA ensembles without SiNPs in 20 mM Tri-HCl, 100 mM NaCl, 5 mM $MgCl_2$, pH 8.0. Absorbance changes at 260 nm versus temperature were collected at a heating rate of 1.5°C·min^{-1}.

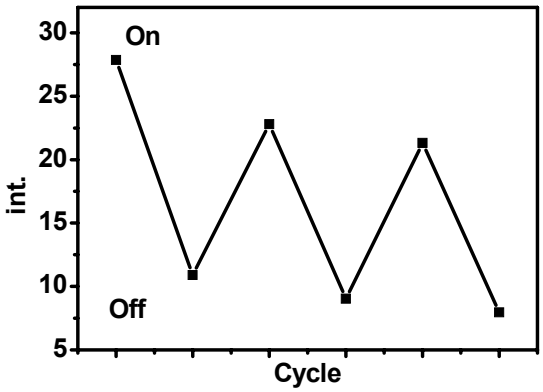


Figure S6. Reversible cycling of fluorescence emission monitored at 525 nm in the

absence and presence of DNA ensemble. The SiNPs were heated, washed, centrifuged, and redispersed after each addition of input strands.

Table S1 Truth table for the concatenated AND gates

	Input B	Input C	Input D	Output
1	0	0	0	0
2	1	0	0	0
3	0	1	0	0
4	0	0	1	0
5	1	1	0	0
6	1	0	1	0
7	0	1	1	0
8	1	1	1	1

Table S2 Truth table for the keypad lock system upon varying the sequence of the B, C, D input signals.

	Input 1	Input 2	Input 3	Output
1	B	C	D	1
2	B	D	C	0
3	C	B	D	0
4	C	D	B	0
5	D	B	C	0
6	D	C	B	0