Supporting Information

Integration of Graphene Oxide and DNA as Universal Platform for Multiple Arithmetic Logic Units

Kun Wang, Jiangtao Ren, Daoqing Fan, Yaqing Liu,* and Erkang Wang*

EXPERIMENTAL SECTION

Materials:

Sequences of DNA strands were listed in the following. DNA oligonucleotides were synthesized by Shanghai Sangon Biotechnology Co (Shanghai, China). DNA oligonucleotide solutions were prepared by dissolving in Tris-HCl buffer (20 mM Tris-HCl, 200 mM KCl, 10 mM MgCl₂, pH 8.0) and quantified by measuring UV-visible absorption spectroscopy at 260 nm. NMM was purchased from Porphyrin Products (Logan, UT, USA). All the other chemicals were purchased from Aladin (Shanghai, China) and used as received without further purification. GO was prepared according to a modified Hummer's method.¹ All other chemicals not mentioned here were of analytical reagent grade and used as received. Milli-Q water (18.2 M Ω) was used throughout.

Table 1: DNA sequences used in this work

Stands	DNA sequence (form 5'-terminal to 3'terminal)
t-DNA	ATTCGTCACTTTCGTATCACGTTTGTGTGCAAT
HA-1	GGGATATTACGATGAACCAAAACGTTAGACGAAAGTATATAAT
HA-2	ATTATATACAAACGTCTAACGAAATGGTTCATCGTAATATGGGTTTTGGGTTTTGGG
HS-1	CCCAAAACCCAAAACCCCGATGAACCAAACGTTAGACGAAAGTATATAAT
HS-2	ATTATATACAAACGTCTAACGAAAGGTTCATCGGGGTTTTGGGTTTTGGGTTTTGGG

To find the available DNA sequences for the developed higher-order logic gates, the designed DNA sequences were firstly mimicked on the website http://mfold.rna.albany.edu/?q=DINAMelt/Twostate- melting and then modified according to the experimental results. The above procedures were repeated until the available DNA sequences were obtained.

Instruments:

Absorbance measurements were performed on a Cary 500 Scan UV/Vis/NIR Spectrophotometer (Varian, USA). Fluorescence measurements were carried out on a Fluoromax-4 spectrofluorometer (Horiba JobinYvon, Inc., NJ, USA). The fluorescence spectra were recorded at room temperature by irradiating FAM at 494 nm and NMM at 399 nm. A JASCO J-810 spectropolarimeter (Tokyo, Japan) was utilized to collect the Circular dichroism (CD) spectra of DNA logic gates.

Logic Gate Operations:

The DNA solutions were heated at 90°C for 10 min and then gradually cooled down to room temperature before conducting experiments. The platform was prepared by mixing GO (6 μ g/ml), *t*-DNA (50 nM) and NMM (1 μ M) for 15 min at room temperature. The used concentrations of the GO and all the inputs were explored by monitoring the fluorescence changing of the system with different DNA concentrations (See Figure S2, S3 and S7 in SI). The concentrations of HA-1, HA-2, HS-1 and HS-2 were 250 nM, 250 nM, 250 nM and 300 nM, respectively. To implement the arithmetic functions, the fluorescence responses of the system were recorded after mixing various inputs with the platform for 30 min. The incubation time was found by monitoring the time-dependent FAM fluorescence signal after adding the input (See Figure S4 and S8 in SI).

Results



Figure S1. (A) FAM fluorescence response of *t*-DNA (50 nM) before and after addition of GO. (B)Timedependent fluorescence changes in GO (6 µg/ml). Buffer: 20 mM Tris-HCl solution (20 mM Tris-HCl, 200 mM KCl, 10 mM MgCl₂, pH 8.0). Excitation wavelength: 494 nm.

As shown in Figure S1 (A), the fluorescence intensity of FAM is significantly quenched once *t*-DNA binding on the GO via noncovalent π - π stacking interaction. The fluorescence intensity of FAM decreases quickly at the beginning and then reaches a plateau, as showed in Figure S1 (B). Here, 15 min was selected as incubation time for preparing of the GO/*t*-DNA logic platform.



Figure S2. FAM fluorescence response of *t*-DNA in the presence of various concentration of GO.

As a quencher and discriminator, the used concentration of GO highly influences the performance of the logic gate. When the concentration of GO is low, the fluorescence of FAM cannot be effectively quenched, leading a strong signal background. On the contrary, the fluorescence of FAM cannot be effectively recovered if the concentration of GO is too high. Here,by monitoring the fluorescence intensity changing of FAM as a function of GO concentration at the wavelength of 521 nm, the optimal concentration of GO is found. The fluorescence intensity of FAM decreases along with increasing the concentration of GO and reached a plateau at 6 μ g/ml GO. Thus, 6 μ g/ml of GO was selected for the following experiments.



Figure S3 (A) The FAM fluorescence restore of GO/*t*-DNA as a function of the HS-1 concentration for the developed half-subtractor. (B) The fluorescence response of FAM as a function of different concentration ratio of the two inputs, HS-1 and HS-2.

As shown in Figure S3 (A), the FAM fluorescence intensity of GO/*t*-DNA increases with the increasing of the concentration of the HS-1 and reaches a plateau up to 250 nM. Thus, 250 nM was selected for the following experiments. For the FAM-related XOR logic gate of HS function, the system presents a low output when the two inputs coexist. To get an optimal low output in this case, the ratio of the inputs' concentration were investigated to reduce signal background. Learned from Figure S3 (B), the FAM fluorescence intensity reaches minimum when the ratio of the two inputs is 1: 1.2. Therefore, the optimal concentrations were found at 250 nM and 300 nM for HS-1 and HS-2, respectively.



Figure S4. The time-dependent fluorescence intensity change of the GO/*t*-DNA complex upon the addition of HS-1.

After the addition of the input, the FAM fluorescence intensity of the GO/*t*-DNA complex increases with time and reaches a plateau in the Figure S4. Here, 30 min was used as the incubation time for the following experiments in HS operation.



Figure S5. The CD spectra for characterizing the DNA structural conversion of the half subtractor (A) and half adder (B).

As shown in Figure S5 (A), the circular dichroism spectrums of the random single strand DNAs, *t*-DNA and HS-1, present low amplitude. The input HS-2 is G-riched and produces obvious negative peak at 261 nm and positive peak at 291 nm, indicating formation of anti-parallel G-quadruplex.²

In the HA logic gate, G-quadruplex was formed due to the hybridization of the two inputs, HA-1 and HA-2. As shown in Figure S5 (B), the circular dichroism spectrum of HA-1 or HA-2 is of relatively low amplitude, indicating that the DNA strands possess no obvious G4 structure. Once the two inputs hybridize together, obvious peaks appear at 262 nm for a negative peak and 294 nm for a positive peak, respectively, indicating formation of anti-parallel G-quadruplex.²



Figure S6. Thermal denaturation curves of the three DNA duplexes (1 μ M): *t*-DNA/HA-1, *t*-DNA/HA-2, HA-1/HA-2. The absorbance spectrum was monitored at 260 nm, the interval temperature was 1°C and the ramp rate was 1°C/min.

Learned from Figure S6, the melting temperature is 44.9° C and 40.0° C for *t*-DNA/HA-1 and *t*-DNA/HA-2, respectively. The highest melting temperature of the duplex of HA-1/HA-2 is 62.1° C, indicating the most stability among the DNA duplexes.³



Figure S7. (A) The FAM fluorescence restore of GO/*t*-DNA as a function of the HA-1 concentration for the developed half-adder. (B) The fluorescence response of FAM as a function of different concentration ratio of the two inputs, HA-1 and HA-2.

As shown in Figure S7 (A), the FAM fluorescence intensity of GO/*t*-DNA increases with the increasing of HA-1 concentration and reaches a plateau up to 250 nM. For the FAM-related XOR logic gate of HA function, the system presents a low output when the two inputs coexisted. To get an optimal low output in this case, the ratio of the inputs' concentrations were investigated to lower signal background. Learned from Figure S6 (B), the FAM fluorescence intensity reaches minimum when the ratio of the two inputs is 1: 1. Therefore, the optimal concentration of 250 nM was used for the two inputs, HA-1 and HA-2.



Figure S8. The time dependent fluorescence changes of the GO/t-DNA complex upon addition of HA-1.

Figure S8 indicates that the FAM fluorescence intensity of the GO/*t*-DNA complex increases with time and then reaches a plateau after addition of the input. Here, 30 min was used as the incubation time for the following experiments about HA operation.

References:

- 1. W. S. Hummers and R. E. Offeman, Journal of the American Chemical Society, 1958, 80, 1339-1339.
- 2. Y. Liu, J. Ren, Y. Qin, J. Li, J. Liu and E. Wang, Chem. Commun., 2012, 48, 802-804.
- 3. R. M. Wartell and A. S. Benight, *Physics Reports*, 1985, 126, 67-107.