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Supporting information

Graphene-nucleic acid biointerface engineered biosensors with tunable dynamic range

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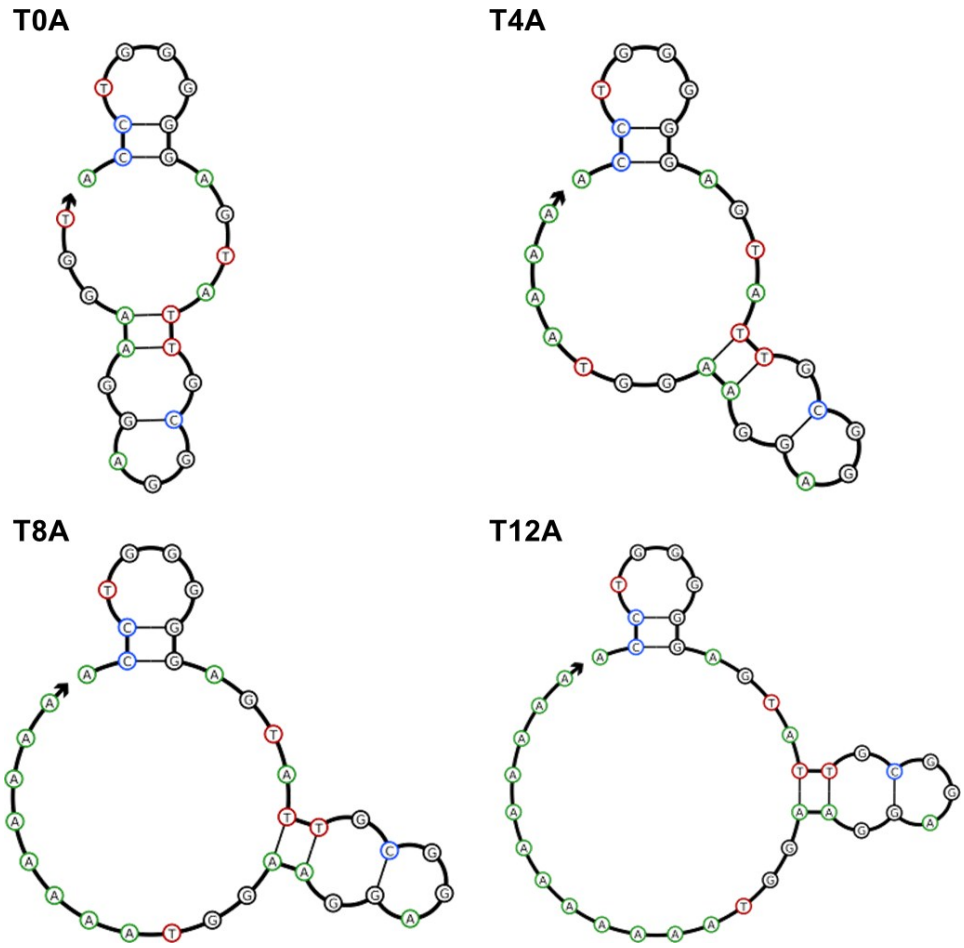

Fig. S1. The secondary structures of the ATP binding aptamer probes (T0A, T4A, T8A and T12A), and the secondary structures were predicted by NUPACK.

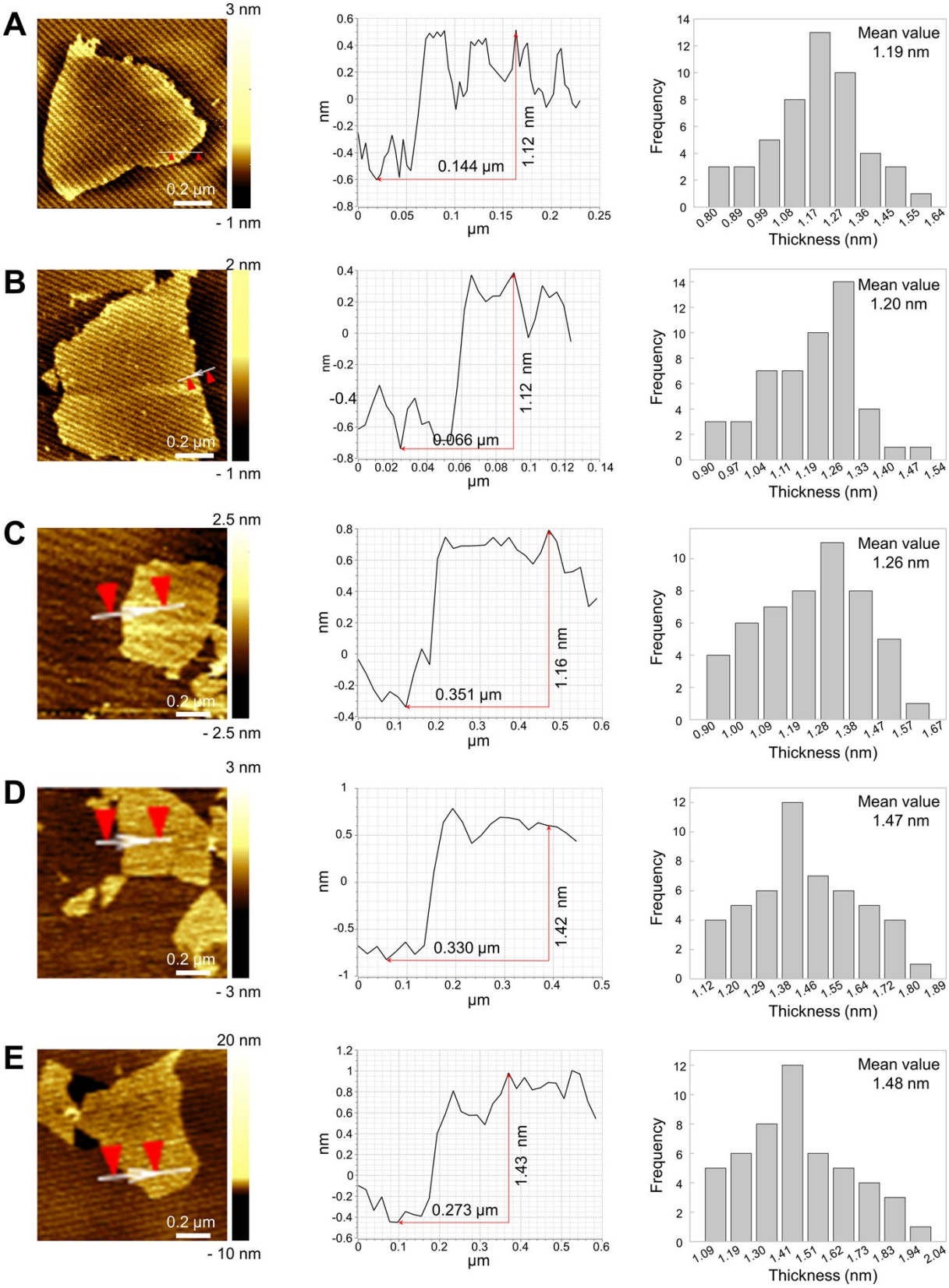

Fig. S2. AFM images and the measured thickness of GO and aptamers-functionalized GO. (A) GO; (B) T0A-functionalized GO; (C) T4A-functionalized GO; (D) T8A-functionalized

GO; (E) T12A-functionalized GO. The final concentration of GO and aptamers with different lengths were 25 μg/mL and 1.5 μM, respectively. As the GO surface was not flat, we estimated the average thickness of GO or GO/aptamer probes by measuring 50 sites.

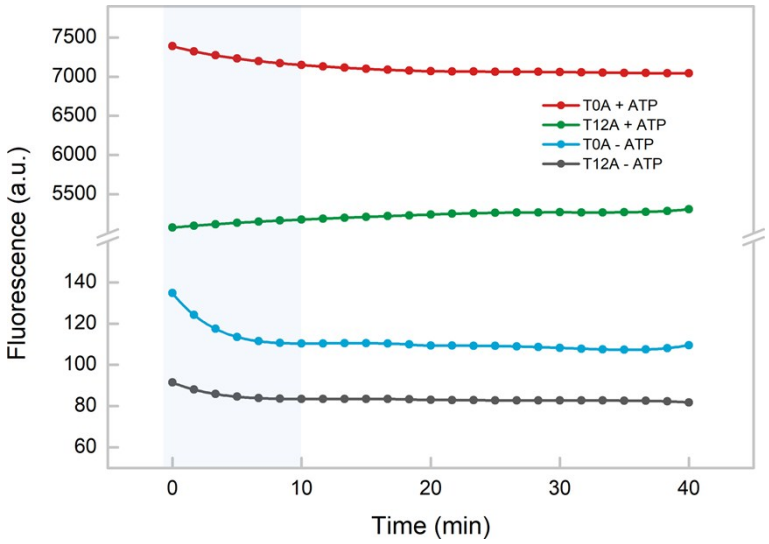

Fig. S3. Investigation of the kinetics of aptamer probe binding in the presence or absence of ATP. The concentrations of ATP, GO and aptamer probes were 2 mM, 25 μg/mL and 150 nM, respectively. The excitation wavelength was set at 480 nm, and the emission wavelength was 522 nm.

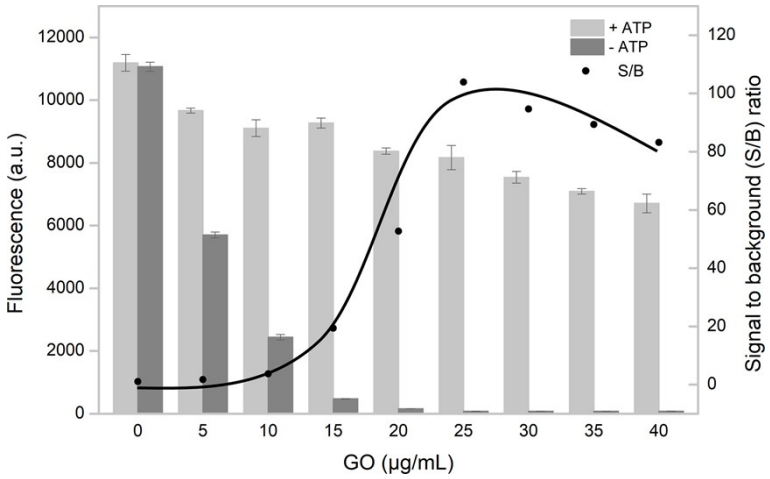

Fig. S4. The fluorescence intensity of atAtpasensor using different concentrations of GO for ATP detection, and the scatter plot of signal-to-background ratio. The concentrations of ATP and aptamer probes were 2 mM and 150 nM, respectively.

Based on the signal-to-background ratio, a concentration of 25 μg/mL GO was used for atAtpasensor.

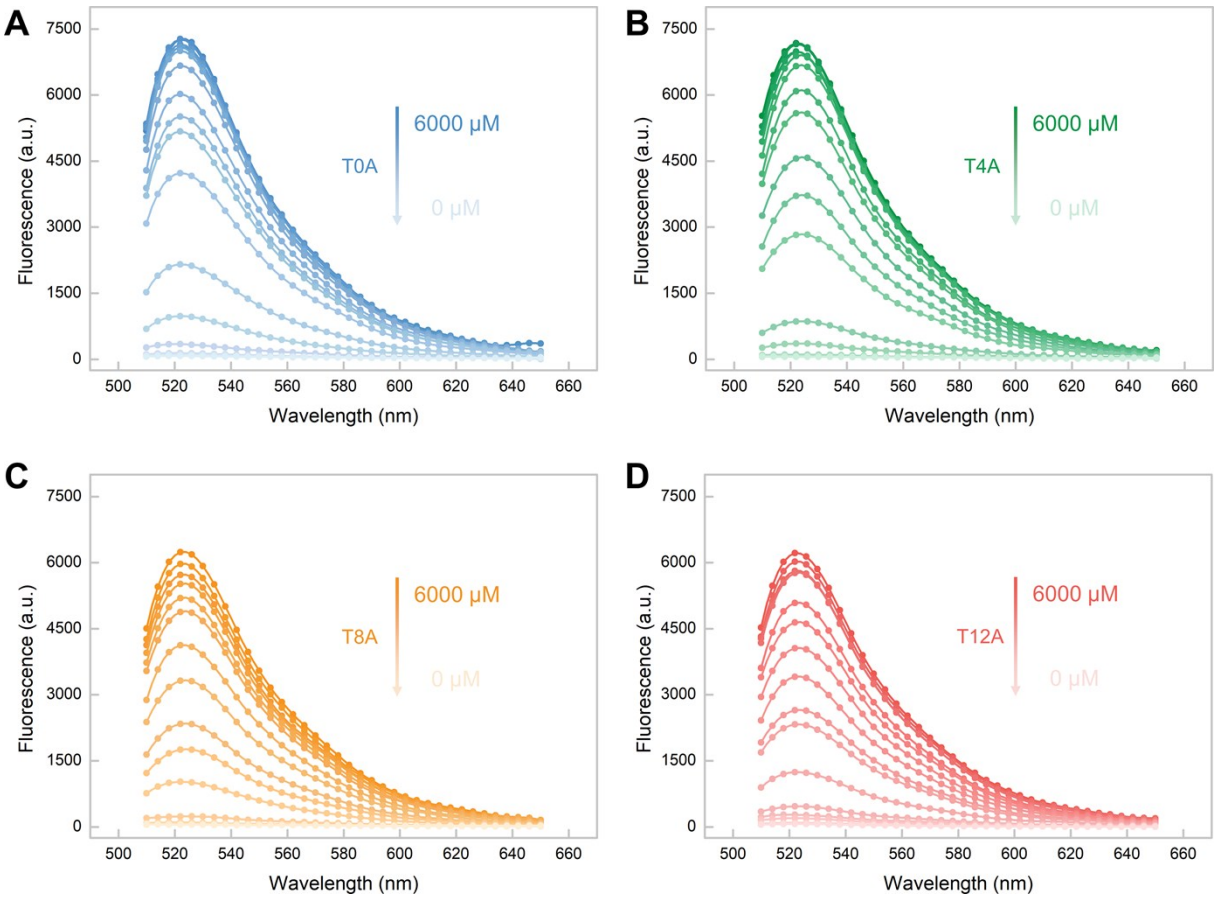

Fig. S5. Typical fluorescence emission spectra of atAtpasensor using T0A (A), T4A (B), T8A (C) and T12A (D) upon the addition of different concentration of ATP range from 0 to 6000 μM. The excitation wavelength was set at 480 nm, and the emission wavelength was 522 nm. The concentration of GO was 25 μg/mL.

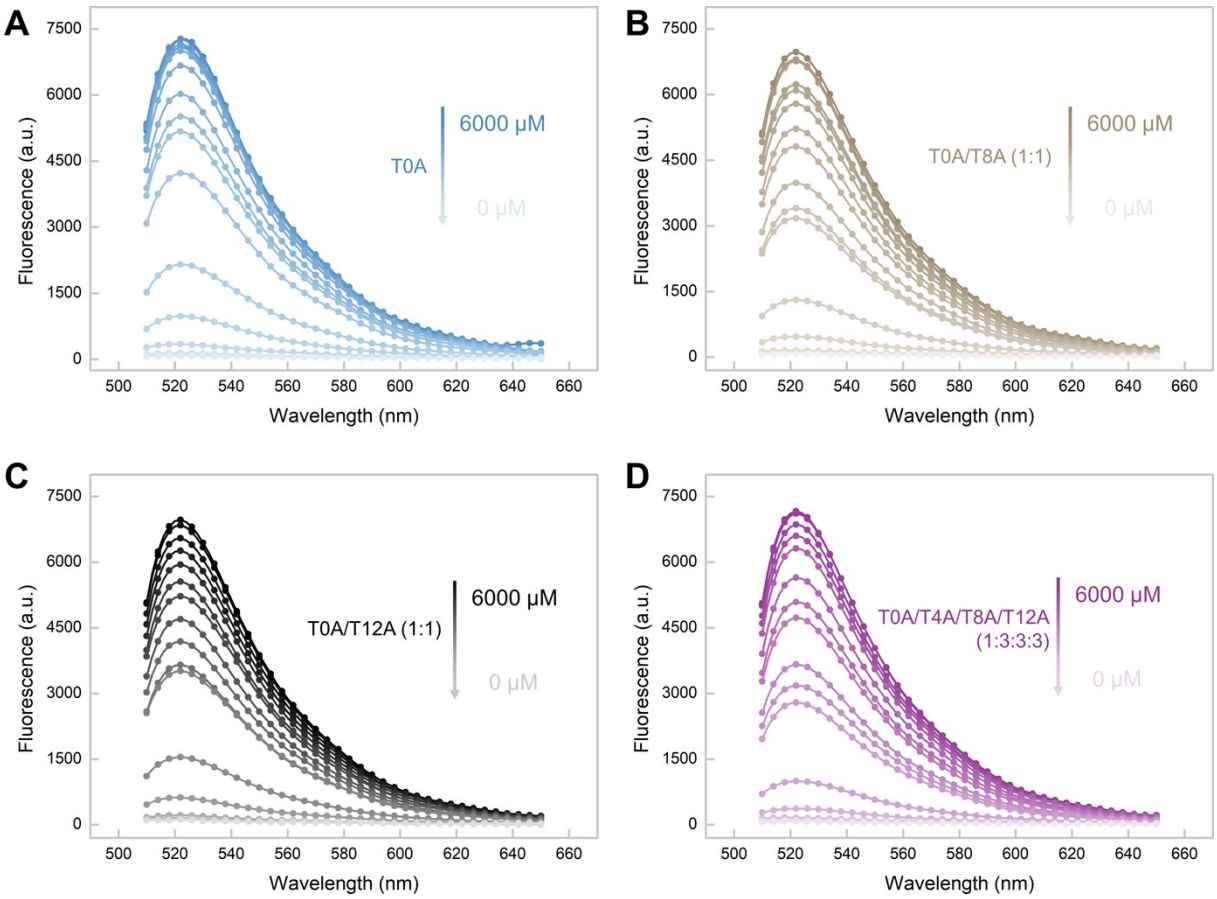

Fig. S6. Typical fluorescence emission spectra of atAtpasensor using T0A (A), T0A/T8A (1:1) (B), T0A/T12A (1:1) (C), and T0A/T4A/T8A/T12A (1:3:3:3) (D) (the content ratio was defined as molar concentrations) upon the addition of different concentration of ATP range from 0 to 6000 μM. The excitation wavelength was set at 480 nm, and the emission wavelength was 522 nm. The concentration of GO was 25 μg/mL.

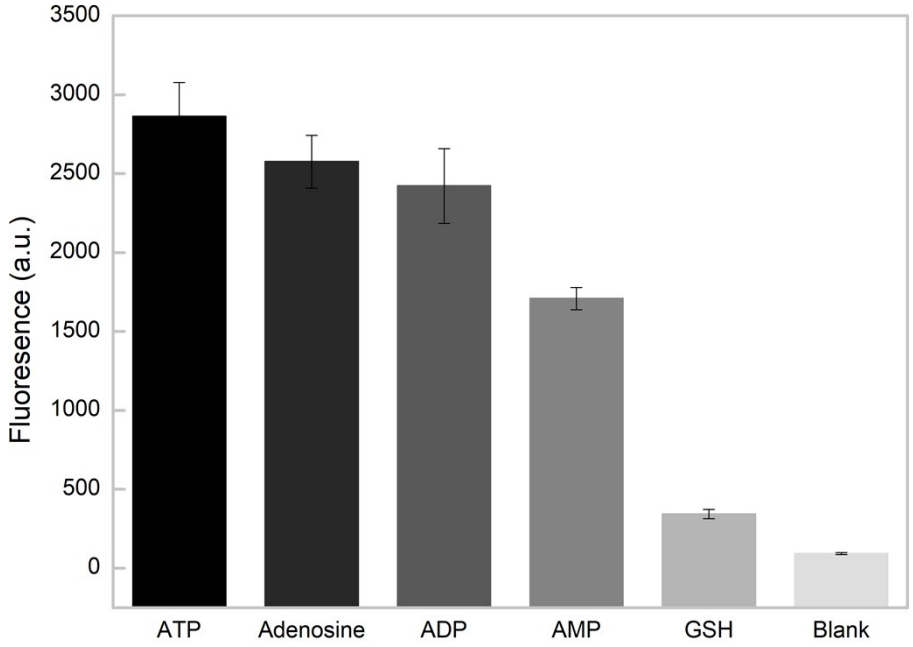

Fig. S7. Fluorescence intensity of atAptasensor in the presence of 250 μM ATP, Adenosine, ADP, AMP, and GSH, respectively. Aptamer probe, T0A/54A/T8A/T12A (1:3:3:3) was selected in this test.

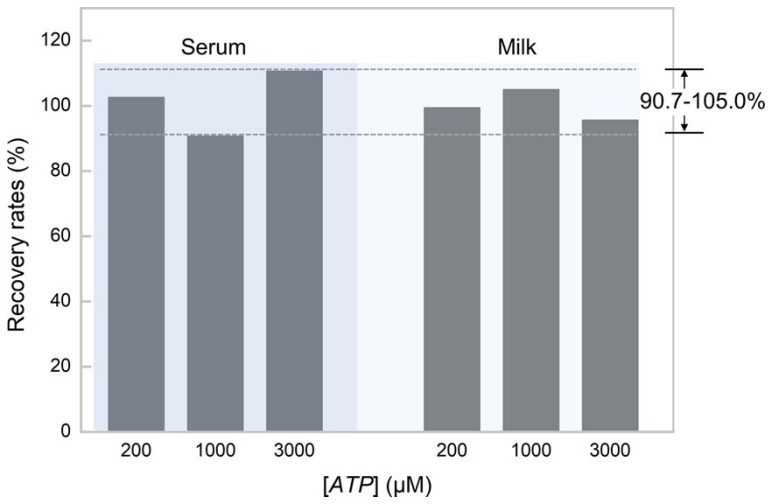

Fig. S8. Recovery of ATP in serum and milk samples. The spiked ATP concentration were 200, 1000 and 3000 μM. The concentration of GO was 25 μg/mL. The concentrations of aptamer probes were 150 nM (15 nM T0A, 45 nM T4A, 45 nM T8A and 45 nM T12A). All real samples were carried for 3 parallel tests.

Table S1. Oligonucleotide sequences

Oligonucleotide	Sequences (5' to 3')
T0A	/FAM/-ACCTGGGGGAGTATTGCGGAGGAAGGT
T4A	/FAM/-ACCTGGGGGAGTATTGCGGAGGAAGGTAAAA
T8A	/FAM/-ACCTGGGGGAGTATTGCGGAGGAAGGTAAAAAAAA
T12A	/FAM/-ACCTGGGGGAGTATTGCGGAGGAAGGTAAAAAAAAAAA

Table S2. Comparison of the fluorescent methods based on aptamer for ATP detection

Detection method	Assay time	Temperature	LOD (μM)	Dynamic range (μM)	samples	Ref.
Berberine based label-free aptamer, AuNRs-RQD Labeled aptamer and AgNP-CD FRET	20 min	37 ℃ and R.T.	3.5, 3.6 and 3.8	10 – 50	Human serum	*Anal. Bioanal. Chem., 2019, 411, 1319*
Two G-rich split ATP aptamer	1.5 min	R.T.	0.002	0.1 - 120	Human serum	*Biosens. Bioelectron., 2019, 134, 36*
Label-free AIE fluorescent probe	10 min	R.T. and 45 ℃	24	100 - 1000	None	*Sensor. Actuat. B-Chem., 2016, 230, 556*
GO-based and Cryonase-Assisted Signal Amplification	30 min	37 ℃	0.0225	0 – 0.1	Serum	*Microchim. Acta, 2019, 186, 494*
Label-Free Fluorescence Polarization Strategy	115 min	20 ℃, 37 ℃	0.0344	0.067 – 26.7	Serum	*Anal. Chem., 2018, 90, 13708*
PEI-CDs based aptasenors	100 min	90℃, R.T., 37 ℃	0.013	30 - 470	Serum	*Microchim. Acta, 2019, 186, 717*
Interchain staudinger reaction based ATP sensing platform	50 min	R.T.	3.25	20 - 100	None	*Talanta, 2018, 178, 282*
Zn^{2+}-modulated lcys-CdTe QDs based aptasensors	25 min	R.T.	2.07	5 - 50	Human serum	*Sensor. Actuat. B-Chem., 2015, 220, 433*
Affinity-tunable aptasensors	**30 min**	**R.T.**	**1.07**	**2 - 3500**	**Milk, Serum, *E. coli.***	***This work***

Table S3. Discrimination factor for ATP detection using different aptamer probes

Non-target molecules	T0A	T4A	T8A	T12A	T0A/T8A (1:1)	T0A/T12A (1:1)	T0A/T4A/T8A/T12A (1:3:3:3)
GTP	3.98	5.25	7.42	11.64	4.34	2.99	7.19
CTP	11.82	37.36	43.28	14.84	24.52	11.86	27.92
UTP	16.28	44.05	49.12	15.45	29.08	14.10	28.48