Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

MnO_2 nanosheets based fluorescent sensing platform with organic dyes as probe with excellent analytical properties

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Table S1. Oligonucleotide sequences

Oligonucleotides	Oligonucleotide Sequences (from 5' to 3')
FAM-T15	TTT TTT TTT TTT TTT
A15	AAA AAA AAA AAA AAA
FAM-PmiR	GG CAT TCA CCG CGT GCC TTA
miR124a	UAA GGC ACG CGG UGA AUG CC
FAM-TBA	GGT TGG TGT GGT TGG

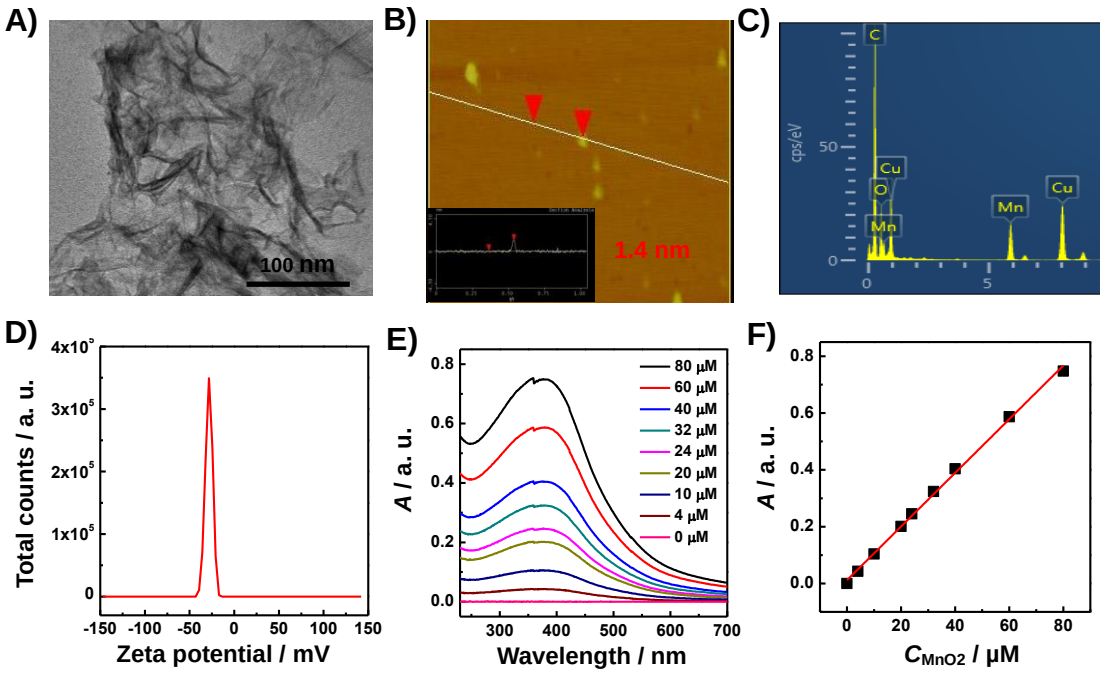

Fig. S1 (A) TEM image of MnO_2 nanosheets. (B) AFM image of MnO_2 nanosheets. (C) Energy dispersive X-ray spectroscope (EDS) spectrum of MnO_2 nanosheets. (D) Zeta potential distribution of MnO_2 nanosheets. (E) UV-vis spectra of MnO_2 nanosheets at various concentrations. (F) Plot of absorbance at 380 nm against the concentration of MnO_2 nanosheets.

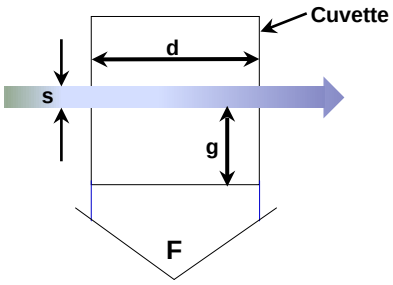

Fig. S2 The parameters used in equation1.

Table S2. IFE of MnO_2 nanosheets on the fluorescence of FAM-T15

MnO_2 (μM)	A_{ex} [a]	A_{em} [b]	CF [c]	F_{obsd} [d]	F_{cor} [e]	E_{obsd} [f]	E_{cor} [g]
0	0.006	0.004	1.008	1197	1207	0	0
4	0.031	0.023	1.058	1127	1193	0.0584	0.0116
10	0.060	0.045	1.119	982.0	1099	0.1796	0.0896
20	0.114	0.087	1.241	783.6	972.0	0.3453	0.1946
30	0.138	0.099	1.290	621.5	802.1	0.4807	0.3355
40	0.181	0.132	1.398	464.5	649.0	0.6119	0.4623
50	0.222	0.164	1.510	339.2	512.2	0.7166	0.5756
60	0.260	0.193	1.619	229.8	372.1	0.8080	0.6917
80	0.332	0.246	1.841	80.16	147.6	0.9330	0.8777
100	0.400	0.298	2.078	21.65	45.05	0.9819	0.9626

[a] A_{ex} is the absorbance of FAM-T15 with the addition of MnO_2 nanosheets at 490 nm. [b] A_{em} is the absorbance of FAM-T15 with the addition of MnO_2 nanosheets at 522 nm. [c] Corrected factor (CF) was calculated as F_{cor}/F_{obsd}. [d] F_{obsd} is the measured fluorescence intensity of FAM-T15 with the addition of MnO_2 nanosheets at 522 nm. [e] F_{cor} is the corrected fluorescence intensity with eq.1 by removing IFE from the measured fluorescence intensity (i.e., F_{obsd}). [f] $E_{obsd}=1-F_{obsd}/F_{obsd,0}$. $F_{obsd,0}$ and F_{obsd} are the observed fluorescence intensities of FAM-T15 in the absence and presence of MnO_2 nanosheets, respectively. [g] $E_{cor}=1-F_{cor}/F_{cor,0}$. $F_{cor,0}$ and F_{cor} are the corrected fluorescence intensities of FAM-T15 in the absence and presence of MnO_2 nanosheets, respectively.

Table S3. IFE of MnO_2 nanosheets on the fluorescence of FAM-T15/A15

MnO_2 (μM)	A_{ex} [a]	A_{em} [b]	CF [c]	F_{obsd} [d]	F_{cor} [e]	E_{obsd} [f]	E_{cor} [g]
0	0.007	0.004	1.0099	1083	1093	0	0
4	0.026	0.018	1.0472	1018	1066	0.0600	0.02537
10	0.055	0.04	1.1072	946.7	1048	0.1258	0.04171
20	0.098	0.071	1.1996	846.6	1015	0.2182	0.07150
30	0.146	0.107	1.3125	742.9	975.1	0.3140	0.1085
40	0.196	0.147	1.4436	639.4	923.0	0.4096	0.1560
50	0.236	0.177	1.5535	567.8	882.0	0.4757	0.1935
60	0.272	0.204	1.6584	506.5	840.0	0.5323	0.2320
80	0.361	0.277	1.9573	381.2	746.1	0.6480	0.3178
100	0.424	0.32	2.1767	299.3	651.5	0.7236	0.4043

[a] A_{ex} is the absorbance of FAM-T15/A15 with the addition of MnO_2 nanosheets at 490 nm. [b] A_{em} is the absorbance of FAM-T15/A15 with the addition of MnO_2 nanosheets at 522 nm. [c] Corrected factor (CF) was calculated as F_{cor}/F_{obsd}. [d] F_{obsd} is the measured fluorescence intensity of FAM-T15/A15 with the addition of MnO_2 nanosheets at 522 nm. [e] F_{cor} is the corrected fluorescence intensity with eq.1 by removing IFE from the measured fluorescence intensity (i.e., F_{obsd}). [f] $E_{obsd}=1-F_{obsd}/F_{obsd,0}$. $F_{obsd,0}$ and F_{obsd} are the observed fluorescence intensities of FAM-T15/A15 in the absence and presence of MnO_2 nanosheets, respectively. [g] $E_{cor}=1-F_{cor}/F_{cor,0}$. $F_{cor,0}$ and F_{cor} are the corrected fluorescence intensities of FAM-T15/A15 in the absence and presence of MnO_2 nanosheets, respectively.

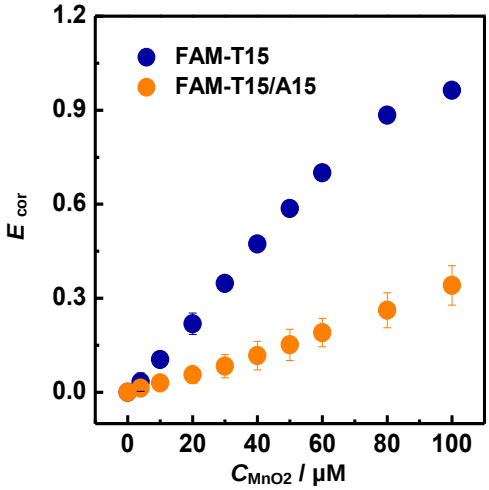

Fig. S3 Corrected suppressed efficiency (E_{cor} = 1-F/F_0) of FAM-T15 (blue dots), FAM-T15 (20 μL, 40 nM) after hybridization with A15 (40 μL, 80 nM) (orange dots), with the presence of different concentrations of MnO_2 nanosheets. *CF* is the corrected factor listed in Table S1 and S2. F_0 and F are the corrected fluorescence intensities of FAM-T15 (20 μL, 40 nM), and FAM-T15 (20 μL, 40 nM) after hybridization with A15 (40 μL, 80 nM), with the presence of MnO_2 nanosheets. Excitation wavelength, 490 nm. Emission wavelength, 522 nm.

Fluorescence anisotropy measurement of MnO_2 nanosheets towards FAM, FAM-T15, and FAM-T15/A15.

By using fluorescence anisotropy measurements, the binding of target molecules will yield a significant change in the rotational diffusion rates of the labeled dyes, resulting in detectable changes in their anisotropy values. According to the literatures,[1,2] the anisotropy (r) is defined as $r = (I_{VV}\text{-}GI_{VH})/(I_{VV} + 2GI_{VH})$. Where I is the measured maximum fluorescence intensity at 522 nm, the subscripts V and H refer to the orientation (vertical or horizontal) of the polarizer for the intensity measurements, with the first subscript indicating the position of the excitation polarizer and the second for the emission polarizer, and $G = I_{HV}/I_{HH}$. In this case, as shown in Fig. S4, addition of MnO_2 nanosheets to FAM solution produces negligible change in anisotropy. This illustrates that the binding of MnO_2 nanosheets to FAM are relatively too weak to hinder the rotation of FAM (Fig. S4, olive dots and orange dots). In contrast, the anisotropy value (r) of FAM-T15 (~ 0.03, Fig. S4, blue dots) was significantly increased when MnO_2 nanosheets was introduced (~ 0.09, Fig. S4, red dots), suggesting a strong and rapid adsorption of FAM-T15 onto MnO_2 nanosheets. This efficient adsorption was due to the strong Van der Waals interaction between the nucleobases and MnO_2 nanosheets. Moreover, in the presence of target A15, the fluorescence anisotropy value varied from ~ 0.09 (Fig. S4, red dots) for FAM-T15 in the presence of MnO_2 nanosheets to ~ 0.05 (Fig. S4, black dots) for FAM-T15/A15 in the presence of MnO_2 nanosheets, this was probably due to the negatively charged FAM-T15/A15 brings a change of DNA conformation, leading to desorption of FAM-T15/A15 from the surface of MnO_2 into the solution.

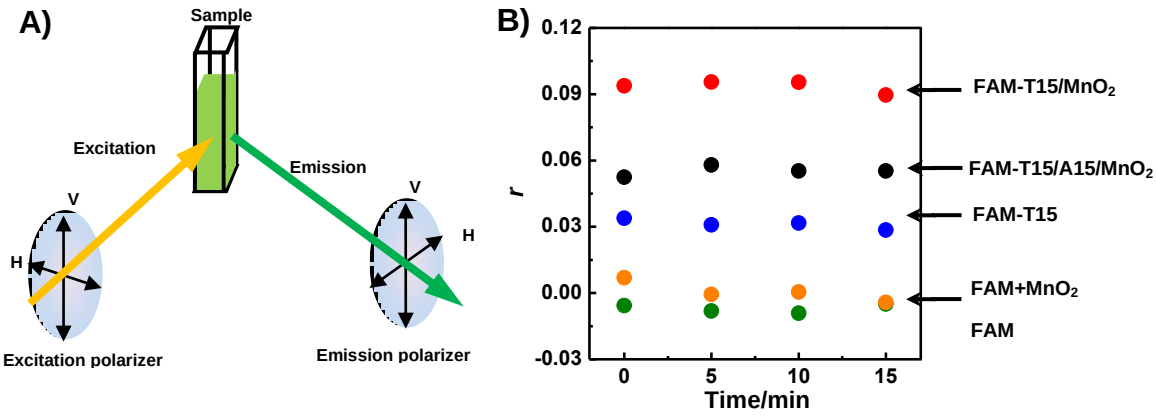

Fig. S4 (A) Schematic diagram for the measurements of fluorescence anisotropy. V (vertical) and H (horizontal) indicate the orientation of the excitation and emission polarizers, respectively. (B) Fluorescence anisotropy value (*r*) of FAM (2 μL, 20 nM, olive dots), FAM-T15 (2 μL, 20 nM, blue dots), FAM (2 μL, 20 nM) with the addition of MnO_2 nanosheets (60 μL, 60 μM, orange dots), FAM-T15 (2 μL, 20 nM) with the addition of MnO_2 nanosheets (60 μL, 60 μM, red dots), and FAM-T15 (2 μL, 20 nM) in the presence of MnO_2 nanosheets (60 μL, 60 μM) and after hybridization with A15 (10 μL, 100 nM) (black dots). Excitation wavelength, 490 nm. Emission wavelength, 522 nm.

Selectivity of MnO_2 nanosheets-based sensing platform towards thrombin

To evaluate the selectivity of FAM-TBA for thrombin with the MnO_2 nanosheets-based sensing platform, different kinds of species that were considered to possibly interfere with thrombin sensing were separately added into the aqueous solution of FAM-TBA. As displayed in Fig. S5A, the addition of each kind of species results in almost no change in fluorescence, as compared with the addition of thrombin (10 μM). As depicted in Fig. S5B, the histogram of relative fluorescence intensity of FAM-TBA towards thrombin and non-target clearly shows that this platform possesses a high selectivity over other analytes.

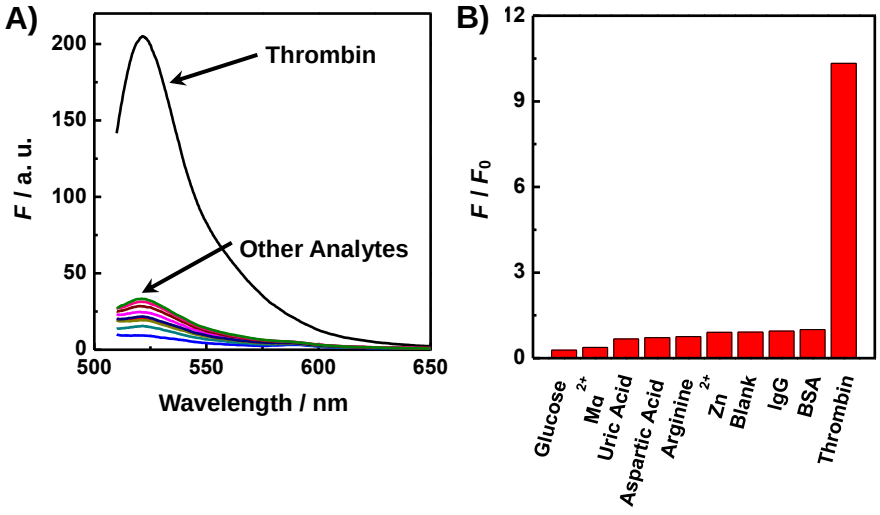

Fig. S5 (A) Fluorescence spectra of FAM-TBA (4 μL, 40 nM) after incubation with glucose (100 μM, olive curve), Mg^{2+} (100 μM, navy curve), uric acid (100 μM, pink curve), aspartic acid (100 μM, dark cyan curve), arginine (100 μM, dark yellow curve), Zn^{2+} (100 μM, wine curve), blank (red curve), lgG (1 μM, magenta curve), BSA (1 μM, blue curve), and thrombin (10 μM, black curve), respectively, after the addition of MnO_2 nanosheets (60 μL, 60 μM). (B) Histogram of F/F_0 at 522 nm obtained from Fig. S5A. F_0 and F denote the intensities of FAM-TBA (4 μL, 40 nM) and MnO_2 nanosheets (60 μL, 60 μM) in the absence and presence of analytes, respectively. Excitation wavelength, 490 nm. Emission wavelength, 522 nm.

REFERENCES

1 J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, 1999.

2 J. H. Liu, C. Y. Wang, Y. Jiang, Y. P. Hu, J. S. Li, S. Yang, Y. H. Li, R. H. Yang, W. H. Tan and C. Z. Huang, *Anal. Chem.*, 2013, **85**, 1424-1430.