

Electronic Supplementary Material (ESI) for New Journal of Chemistry

## **Development of manganese dioxide-based nanoprobe for fluorescent detection and imaging of glutathione**

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## Experimental section

### Materials

All chemicals were purchased from Sigma-Aldrich if not specially mentioned. Fetal Bovine Serum (FBS), penicillin/streptomycin antibiotics (P/S), and cell culture medium were purchased from Gibco™ Thermo Fisher Scientific Inc.

### MTT assay

Cell viability experiments were conducted by MTT assay in 96-well plates. MnO<sub>2</sub>-PEI-FITC nanoprobees were freshly prepared in DMEM (10% PBS, 1% P/S). Typically, CT26 cells were seeded at the density of 1.0 × 10<sup>4</sup> and 2.0 × 10<sup>4</sup> cells per well and incubated overnight at 37°C with 5% CO<sub>2</sub> until around 50% (for 24 h NP treatment) and 70% (for 4 h NP treatment) cell confluence, respectively. Culture medium was then replaced with 100 μL of fresh medium containing the nanoprobees at a series of concentrations (0, 2, 4, 6, 8, 10, 20, 50, and 100 μg/mL). The cell viability was determined after 4 and 24 h incubation respectively, using the standard MTT assay protocol. Typically, culture medium was replaced by 100 μL of MTT solution (0.5 mg/mL in blank DMEM medium) in each well, followed by incubating for another 4 h in a cell incubator at 37°C with 5% CO<sub>2</sub>. MTT solution was removed and then 100 μL of DMSO was added to dissolve the MTT formazan for 10 min. The absorbance at 570 nm was measured in a microplate reader (Biotek, Winooski, VT) to estimate the cell viability.

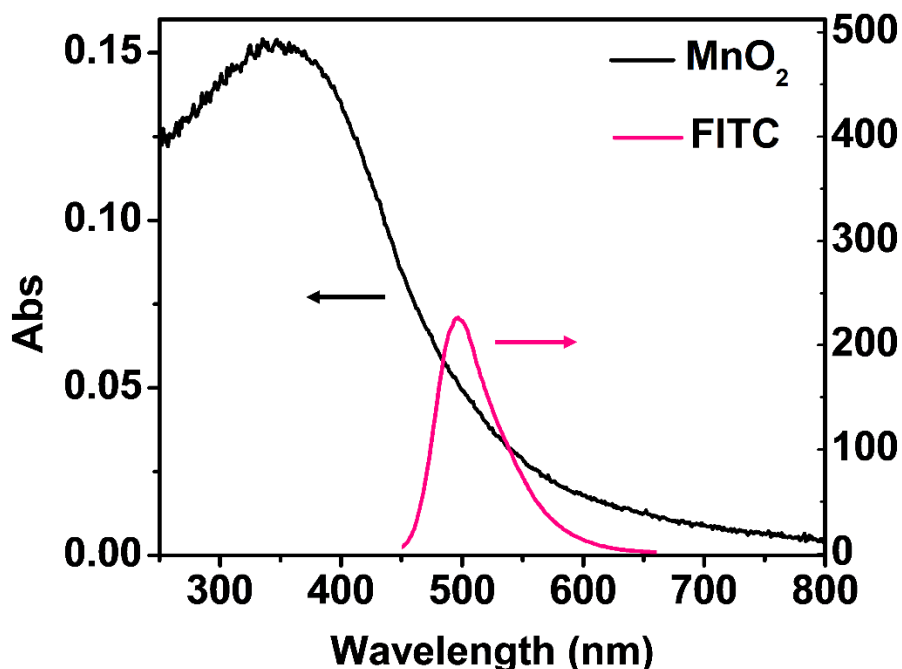


Fig. S1. Absorption (black) spectrum of MnO<sub>2</sub> nanosheet and emission (red) spectrum of FITC.

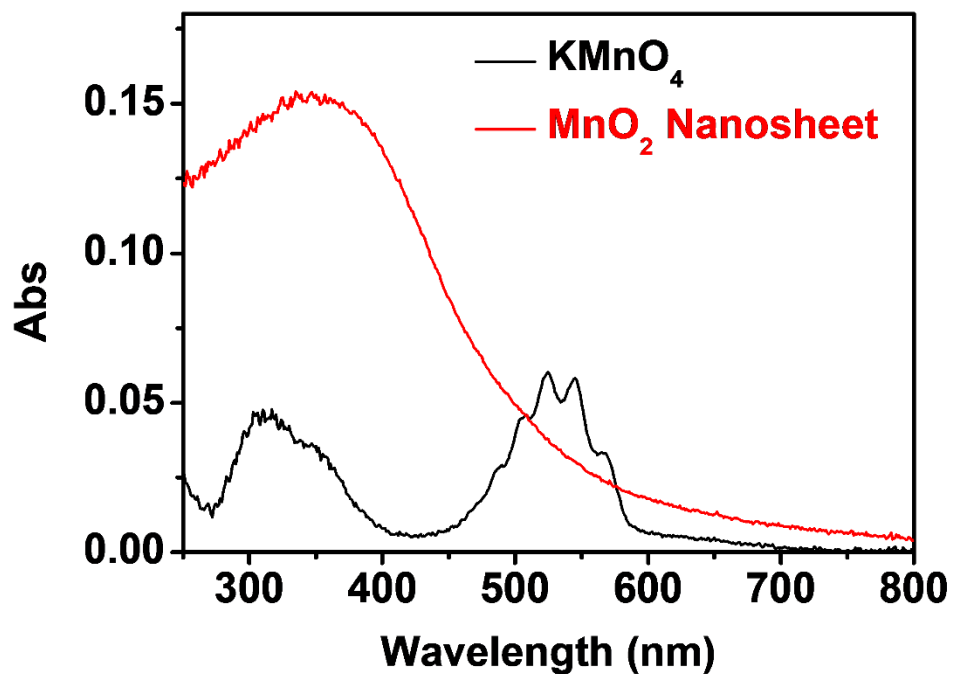


Fig. S2. Absorption spectra of  $\text{KMnO}_4$  and  $\text{MnO}_2$  nanosheet.

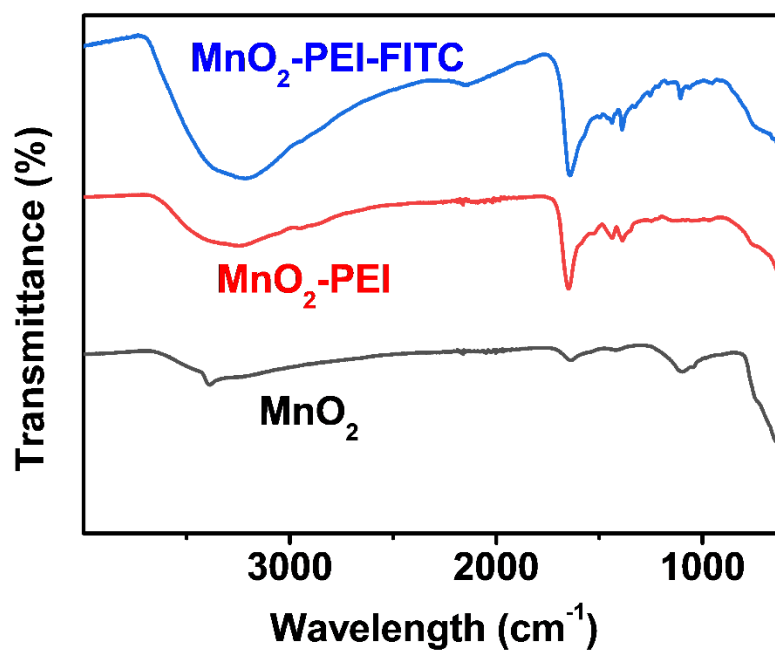


Fig. S3. FTIR spectra of  $\text{MnO}_2$ ,  $\text{MnO}_2$ -PEI, and  $\text{MnO}_2$ -PEI-FITC.

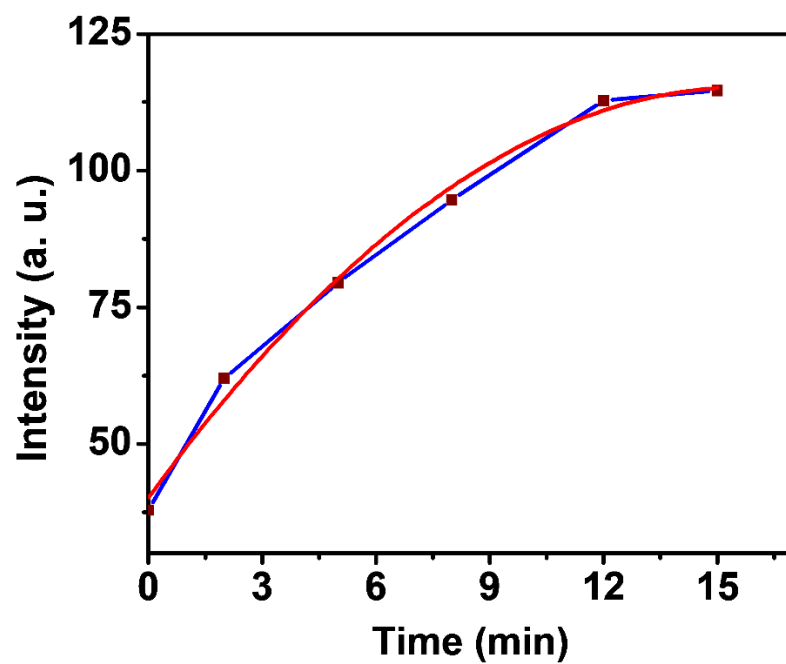


Fig. S4. Time-dependent fluorescence response of MnO<sub>2</sub>-PEI-FITC to 15 μM GSH.

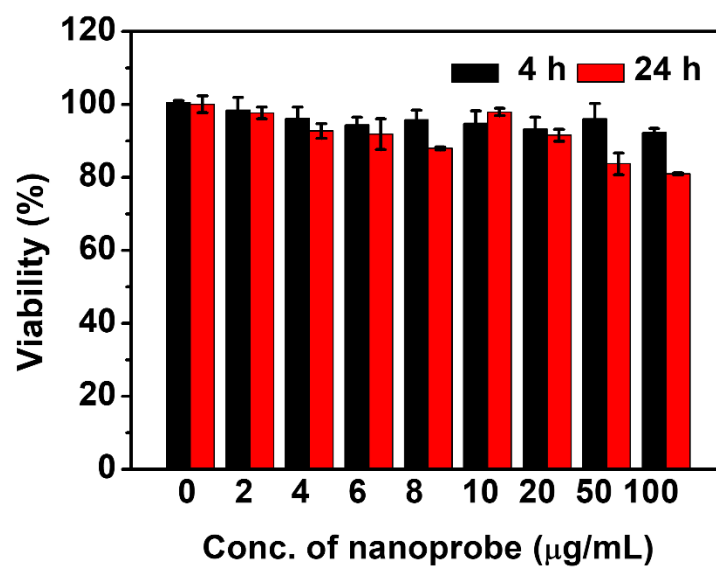
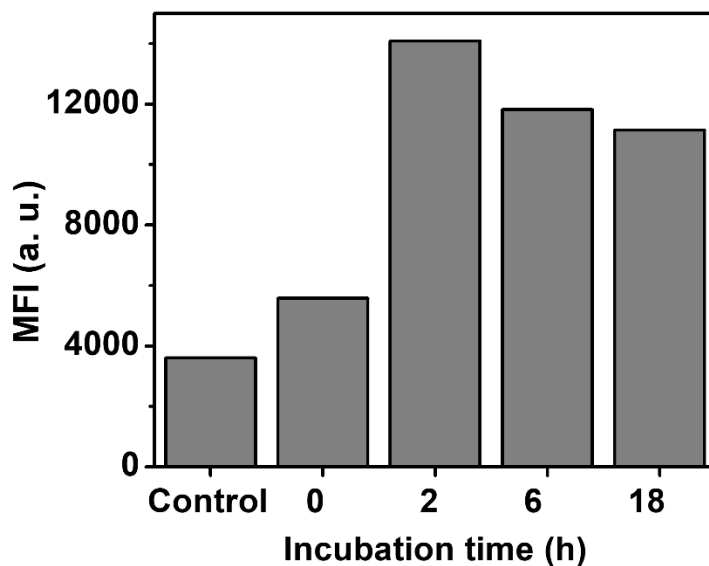
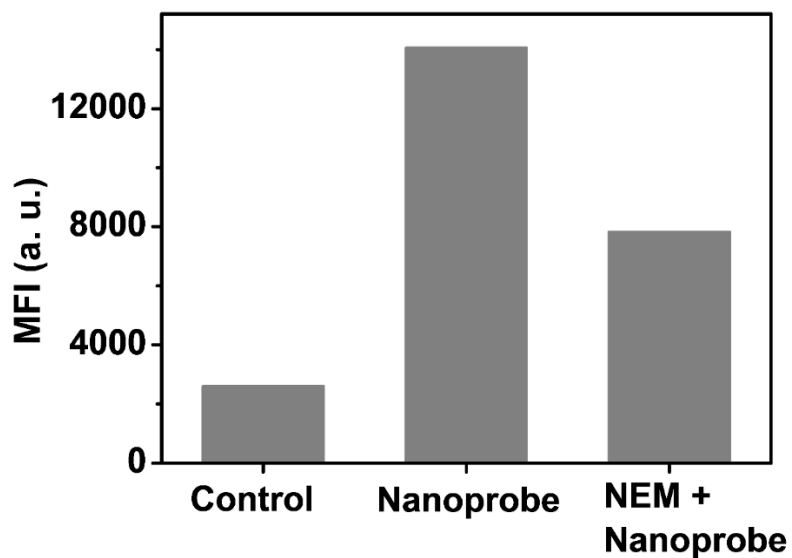


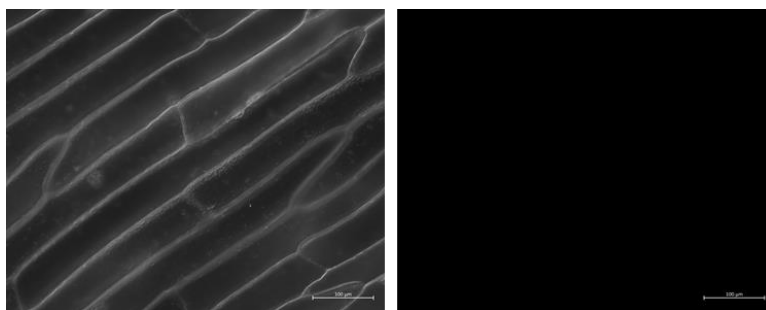
Fig. S5. MTT cytotoxicity analysis of MnO<sub>2</sub>-PEI-FITC to CT26 colon cancer cells.



**Fig. S6.** Flow cytometry analyses of yeast cells incubated with MnO<sub>2</sub>-PEI-FITC for 0, 2, 6, and 18 h.



**Fig. S7.** Mean fluorescence intensity (MFI) of free yeast cells incubated by nanoprobe with and without NEM treatment.



**Fig. S8.** DIC and fluorescence images of onion inner-layer epidermal tissues treated with NEM (5 mM) for 2 h and stained with MnO<sub>2</sub>-PEI-FITC nanoprobe for another 2 h. Scale bars are 100 μm.

**Table S1.** Comparison of the MnO<sub>2</sub>-PEI-FITC nanoprobe with other reported probes for GSH detection

Method	Nanoprobe	$\lambda_{ex}/\lambda_{em}$	Linearity range $\mu$ M	Limit of detection ( $\mu$ M)	Detection time (min)	Application	Ref.
Colorimetry	Gold nanoparticles (AuNPs)	200/700 nm	0.04-0.28	-	20	Human serum	(1)
Colorimetry	CuS-polydopamine-Au	-	0.5-100	0.42	30	Human serum and cellular GSH levels	(2)
Colorimetry	Gold nanoparticles (AuNPs)	-	0.1-1.0	0.02	5	human serum and urine	(3)
Fluorimetry	SiO <sub>2</sub> Particles	340/430 nm	0.1-10	0.34	20	Dietary supplement	(4)
Fluorimetry	MnO <sub>2</sub> nanosheet- lanthanide-doped upconversion nanoparticles (UCNPs)	NIR 980 nm	-	0.9	180	Cell imaging	(5)
Fluorimetry	MnO <sub>2</sub> -Nanosheet-Modified Two-Photon Mesoporous Silica Nanoparticles (TP-MSNs@MnO <sub>2</sub> )	370/470 nm	0-100	0.2	30	Cell and tissue slices imaging	(6)
Fluorimetry	Sr <sub>2</sub> MgSi <sub>2</sub> O <sub>7</sub>	-	0-100	0.83	60	Cell and mice imaging	(7)
Fluorimetry	AgNP/DNA/TPdye	450/550 nm	1-10	0.3	60	Cell and tissue slices imaging	(8)
Fluorimetry	AuNC@BSA/MnO <sub>2</sub> nanosheets	365/430 nm	0-500	0.02	-	-	(9)
Fluorimetry	Lucigenin-MnO <sub>2</sub> nanosheets	370/500 nm	1-150	0.15	5	Human serum plasma	(10)
Fluorimetry	N-doped graphene quantum dots (NGQDs)-MnO <sub>2</sub> nanocomposite	310/430 nm	0-400	0.000027	8	Human serum	(11)
Fluorimetry	Endoplasmic reticulum (ER)-targeting fluorescent probe	470/500 nm	75-300	0.023	8	Cell imaging	(12)
Fluorimetry	MnO <sub>2</sub> -PEI-FITC	490/518 nm	0-80	0.164	12	Yeast cells and Onion tissue	This work

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