

Electronic Supplementary Information

Turn-on fluorescent glutathione detection based on lucigenin and MnO₂ nanosheets

Mohamed Ibrahim Halawa,^{a,b,c} Fengxia Wu,^{a,d} Muhammad Nadeem Zafar,^{a,e} Islam M. Mostafa,^{a,d} Abubakar Abdussalam,^{a,d} Shuang Han,^{f,*} Guobao Xu^{a,*}

^a State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, P.R. China

^b University of Chinese Academy of Sciences, Beijing 100049, P.R. China

^c Department of Pharmaceutical Analytical Chemistry, Faculty of Pharmacy, University of Mansoura, 35516, Mansoura, Egypt.

^d University of Science and Technology of China, Anhui 230026, China

^e Department of Chemistry, University of Gujrat, Gujrat, 50700 Pakistan

^f College of Applied Chemistry, Shenyang University of Chemical Technology, Shenyang 110142, China

Corresponding Author

* Phone: +86-431-85262747. Fax: +86-431-85262747.

E-mail: guobaoxu@ciac.ac.cn (G. B. Xu), unihanshuang@163.com (S. Han)

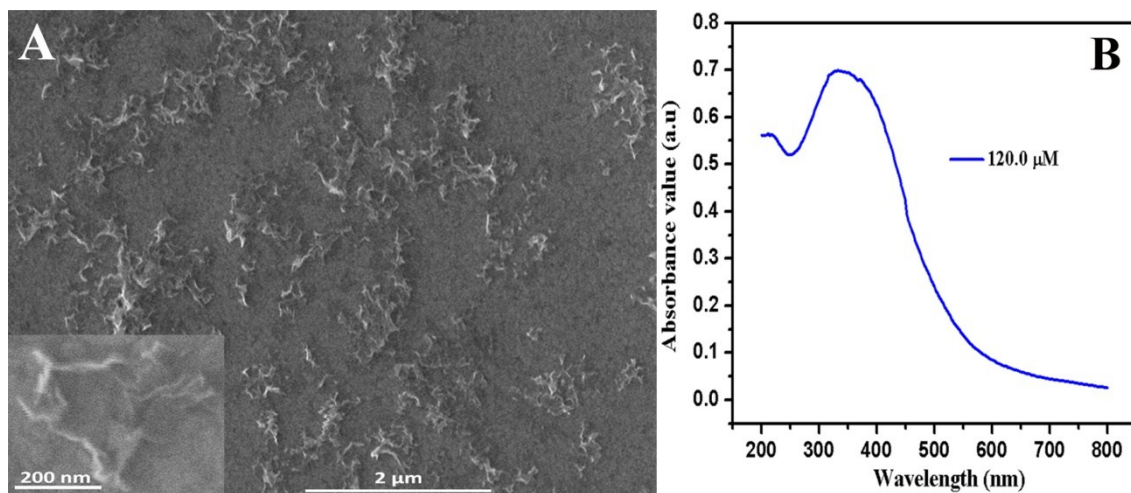


Figure S1. A) SEM images of MnO₂ nanosheets. B) UV-vis absorption spectrum of MnO₂ nanosheets

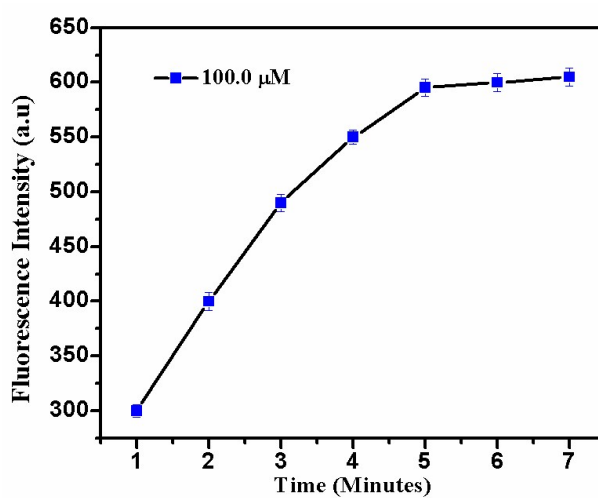


Figure S2. Kinetics of fluorescence recovery by monitoring fluorescence intensity at 500 nm as a function of time of the mixed lucigenin-MnO₂ nanosheets solution in the presence 100.0 μM GSH.

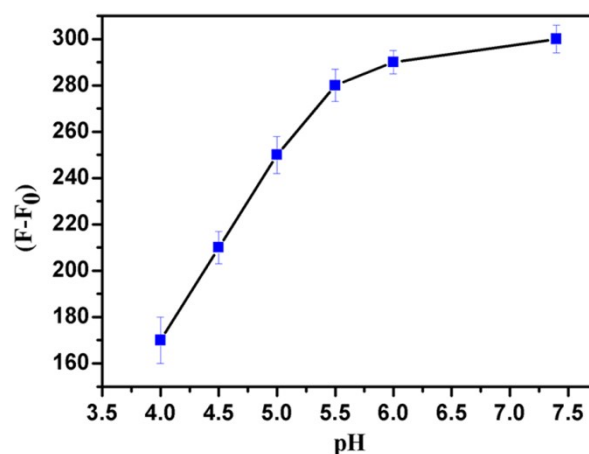


Figure S3. The effect of pH on the recovery of fluorescence intensity for the mixed lucigenin-MnO₂ nanosheets solution in the presence 100.0 μ M GSH.

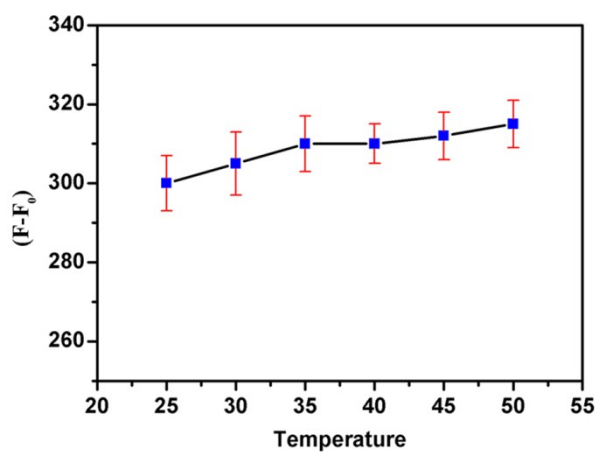


Figure S4. The effect of temperature on the recovery of fluorescence intensity for the mixed lucigenin-MnO₂ nanosheets solution in the presence 100.0 μ M GSH.

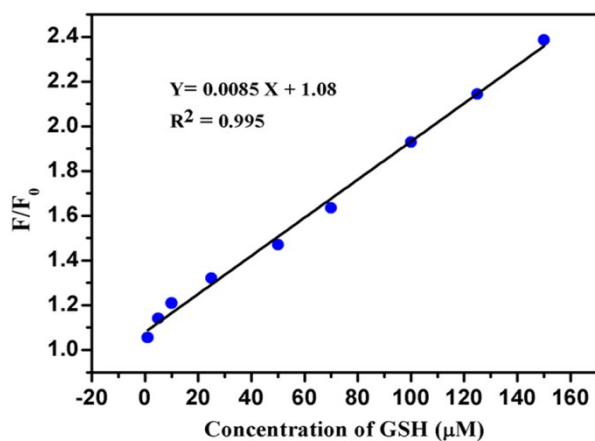


Figure S5. A plot demonstrates the linear relationship between the rate of recovery of fluorescence intensity (F/F_0) and GSH concentrations

Table S1. Fitting results of the fluorescence lifetimes for lucigenin and lucigenin– MnO_2 nanosheets mixture

Sample	$\tau_1(\text{ns})$	$A_1(\%)$	$\tau_2(\text{ns})$	$A_2(\%)$	$\tau_{\text{average}}(\text{ns})$
Lucigenin	9.995	4.517×10^{-3}	20.058	7.5083×10^{-2}	19.45
Lucigenin – MnO_2 nanosheets	2.403	6.566×10^{-3}	19.306	7.757×10^{-2}	18.01

Table S2. Quantum yields and Zeta Potentials of the free-state lucigenin and the Lucigenin-MnO₂ nanosheets conjugate solution in absence and presence of GSH.

	Lucigenin	Lucigenin-MnO ₂ nanosheets	Lucigenin-MnO ₂ Nanosheets-GSH
Quantum Yield (Φ)	0.69	0.31	0.68
Zeta potential (ζ) at pH=7.4	-47.3 mV	-7.21mV	N/A

Table S3. Comparison of the developed method with the other reported methods for the detection of GSH.

Methods	Linearity range μM	Limit of detection (LOD)	Detection time (Minutes)	References
Colorimetry	0.013- 0.8	N/A	20	1
Colorimetry	0.5 –100	0.42	30	2
Colorimetry	0.1–1.0	0.023	5	3
Fluorimetry	0.1- 10	0.34	20	4
Fluorimetry	N/A	0.9	3 hrs	5
Fluorimetry	0-100	0.2	30	6
Fluorimetry	0-100	0.83	1 hr	7
Fluorimetry	1-10	0.8	1 hr	8
Fluorimetry	0-500	4	N/A	9
Fluorimetry	1-150	0.15	5	This work

Table S4. Assay results for GSH detection in diluted human serum samples.

Target	Amount found (μM)	Amount spiked (μM)	Total found (μM)	Recovery (%, n= 3)	RSD (%, n= 3)
GSH	4.05	5.0	8.85	97.84	1.45
		25.0	29.50	101.57	1.88
		100.0	107.01	102.85	2.03
tGSH	4.58	5.0	9.33	97.38	1.81
		25.0	29.62	100.13	2.12
		100.0	108.53	103.78	2.55

References

1. C. Lai, L. Qin, L. Chen, G.-M. Zeng, D.-L. Huang, C. Zhang, P. Xu and M. Cheng, *Int. J. Environ. Anal. Chem.*, 2017, **97**, 71-84.
2. Y. Wang, Y. Liu, F. Ding, X. Zhu, L. Yang, P. Zou, H. Rao, Q. Zhao and X. Wang, *Anal. Bioanal. Chem.*, 2018, **410**, 4805-4813.
3. J.-F. Li, P.-C. Huang and F.-Y. Wu, *RSC Adv.*, 2017, **7**, 13426-13432.
4. P. Nedeljko, M. Turel and A. Lobnik, *J. Sens.*, 2018, **2018**, 9.
5. R. Deng, X. Xie, M. Vendrell, Y.-T. Chang and X. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 20168-20171.
6. H.-M. Meng, Z. Jin, Y. Lv, C. Yang, X.-B. Zhang, W. Tan and R.-Q. Yu, *Anal. Chem.*, 2014, **86**, 12321-12326.
7. N. Li, W. Diao, Y. Han, W. Pan, T. Zhang and B. Tang, *Chem. Eur. J.*, 2014, **20**, 16488-16491.
8. Q. Tang, N. Wang, F. Zhou, T. Deng, S. Zhang, J. Li, R. Yang, W. Zhong and W. Tan, *Chem. Commun.*, 2015, **51**, 16810-16812.
9. S. Lin, H. Cheng, Q. Ouyang and H. Wei, *Anal. Methods*, 2016, **8**, 3935-3940.