## Supplementary materials for

## A visual ratiometric fluorescence sensor for glutathione response based on MnO<sub>2</sub> nanowires as oxidants, quencher and recognition unit

Yu Fan<sup>a,1</sup>, Xin Wang<sup>a,1</sup>, He Huang<sup>a</sup>, Yumeng Yang<sup>a</sup>, Jinlin Guo<sup>a,c</sup>, Shajie Luo<sup>a\*</sup>,

Meilian Zhao<sup>b\*</sup>, Yang Li<sup>b\*</sup>

<sup>a</sup> Chongqing Key Laboratory of Sichuan-Chongqing Co-Construction for Diagnosis and Treatment of Infectious Diseases Integrated Traditional Chinese and Western Medicine, College of Medical Technology, Chengdu University of Traditional Chinese Medicine, Chengdu 611137, China

<sup>b</sup> School of Public Health, Chengdu University of Traditional Chinese Medicine, Chengdu 611137, China

<sup>c</sup> State Key Laboratory of Southwestern Chinese Medicine Resources, School of Pharmacy, Chengdu University of Traditional Chinese Medicine, Chengdu 611137, China

<sup>\*</sup> Corresponding author.

*E-mail address:* <u>liyang@cdutcm.edu.cn</u> (Y. Li), <u>zhaomeilian2009@126.com</u> (M. Zhao), <u>luoshajie@cdutcm.edu.cn</u> (S. Luo)

<sup>&</sup>lt;sup>1</sup> Co-first author.



Fig. S1. (A) and (B) The TEM image of the as-prepared  $MnO_2$  NWs.



**Fig.S2.** (A) UV–vis absorption spectrum of VB<sub>1</sub> and VB<sub>1</sub> + MnO<sub>2</sub> NWs; (B) The time-resolved fluorescence decay curve of RhB and RhB + MnO<sub>2</sub> NWs; (C) UV–vis absorption spectrum of RhB and RhB + MnO<sub>2</sub> NWs; (D) UV–vis absorption spectrum of GSH, MnO<sub>2</sub> NWs and GSH + MnO<sub>2</sub>

NWs; (E) Schematic illustration of  $VB_1$  being oxidized by  $MnO_2$  NWs to  $oxVB_1$ .



Fig. S3. Effects of pH on the ratiometric fluorescent sensor. Plots of I<sub>450</sub>, I<sub>580</sub>, and the ratio value

*I*<sub>580</sub>/*I*<sub>450</sub> versus pH, respectively.



Fig.S4. The linear relationship between the ratio value  $I_{580}/I_{450}$  and L-cysteine concentrations from

500 to 3000  $\mu M.$ 



Fig. S5. (A) Selectivity of the ratiometric fluorescent sensor, a: l-alanine, b: l-phenylalanine, c:
proline, d: methionine, e: glucose, f: NaCl, g: KCl, h: NaHCO<sub>3</sub>, i: NaH<sub>2</sub>PO<sub>4</sub>, j: H<sub>2</sub>O and K: GSH.
(B) Photographs of the ratiometric fluorescent sensor under UV light after addition of different

substances.

Sample	Added (µM)	Detected <sup>a</sup> ( $\mu$ M)	Recovery (%)
whitening capsules	0	$475.9\pm10.5$	_
	500	$998.8 \pm 10.6$	104.6
	1000	$1481 \pm 11.2$	100.5
glutathione tablets	0	$490.0\pm7.7$	_
	500	$1037 \pm 11.3$	109.4
	1000	$1546 \pm 12.3$	105.6

Table S1 Recovery results of GSH in real samples.

 $^{\rm a}$  Average of three determination  $\pm$  SD, n=3

Sample	Present work (µM)	HPLC (µM)
whitening capsules	$475.9 \pm 10.5$	483.9 ± 3.9
glutathione tablets	$490.0\pm7.7$	487.3 ± 6.5

Table S2 Applications of the prepared sensor to the real sample in contrast to HPLC.