Electronic Supplementary Information

Fluorescent and colorimetric determination of glutathione based on the inner filter effect between silica nanoparticle-gold nanoclusters nanocomposites and 3,3',5,5'-tetramethylbenzidine

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Experimental section

1. Synthesis of AuNCs

AuNCs were synthesized according to the method reported by Xie group with a little change.[1] In a round bottom flask with 26.58 mL ultrapure water, the aqueous solutions of $HAuCl_4$ (2.52 mL, 1%) was first added under slowly stirring, and then GSH (0.9 mL, 100 mM) was added and mixed together at 25 °C. The reaction mixture was heated to 70 °C under stirring for 24 h. AuNCs aqueous solution with strongly orange-emitting was formed. The AuNCs solution could be stored at 4 °C for 6 months with good stability.

2. Synthesis of amino-functionalized MSNs

The amino-functionalized MSNs were synthesized by co-condensation in alkaline solution.[2] First, the CTAB (0.5 g) was initially mixed in 200 mL of ultrapure water. Then, NaOH aqueous solution (2 M, 1.75 mL) was slowly dropwise added into the CTAB solution under stirring for 20 min at 80 °C. When the temperature was no longer changing, TEOS (2.5 mL) was slowly dropwise added into the above solution and vigorously stirred for 15 min. After that, APTES (0.5 mL) was added dropwise and vigorously stirred for another 2 h at 80 °C. Lastly, the obtained white precipitates were centrifuged and washed three times with methanol and ultrapure water. In order to remove the excess CTAB, the amino-functionalized MSNs were refluxed in the mixture solution of HCl (9 mL, 37%) and methanol (150 mL) for 10 h at 80 °C. Then, the product was washed thoroughly with methanol and ultrapure water. The collected amino-functionalized MSNs were dried under vacuum for 60 °C overnight.

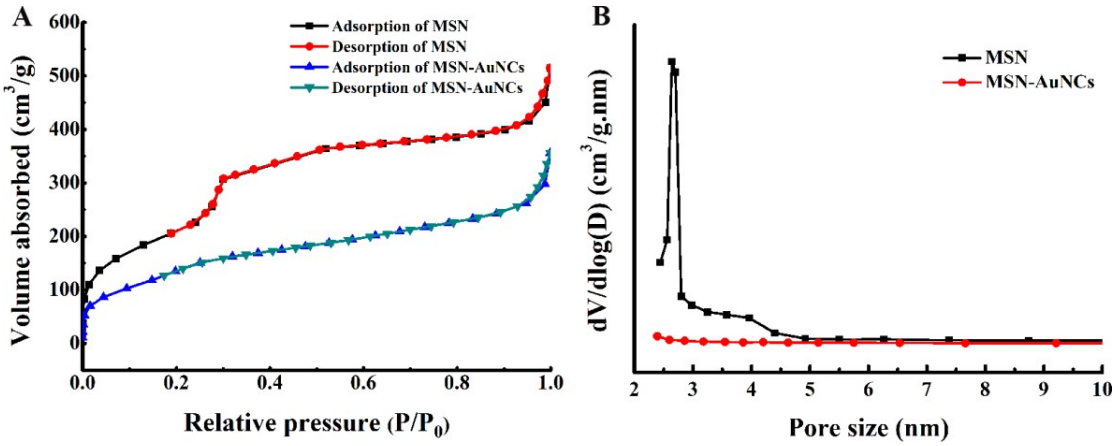

Fig. S1. (A) N_2 adsorption-desorption isotherm and (B) pore size distributions of MSN and MSN-AuNCs.

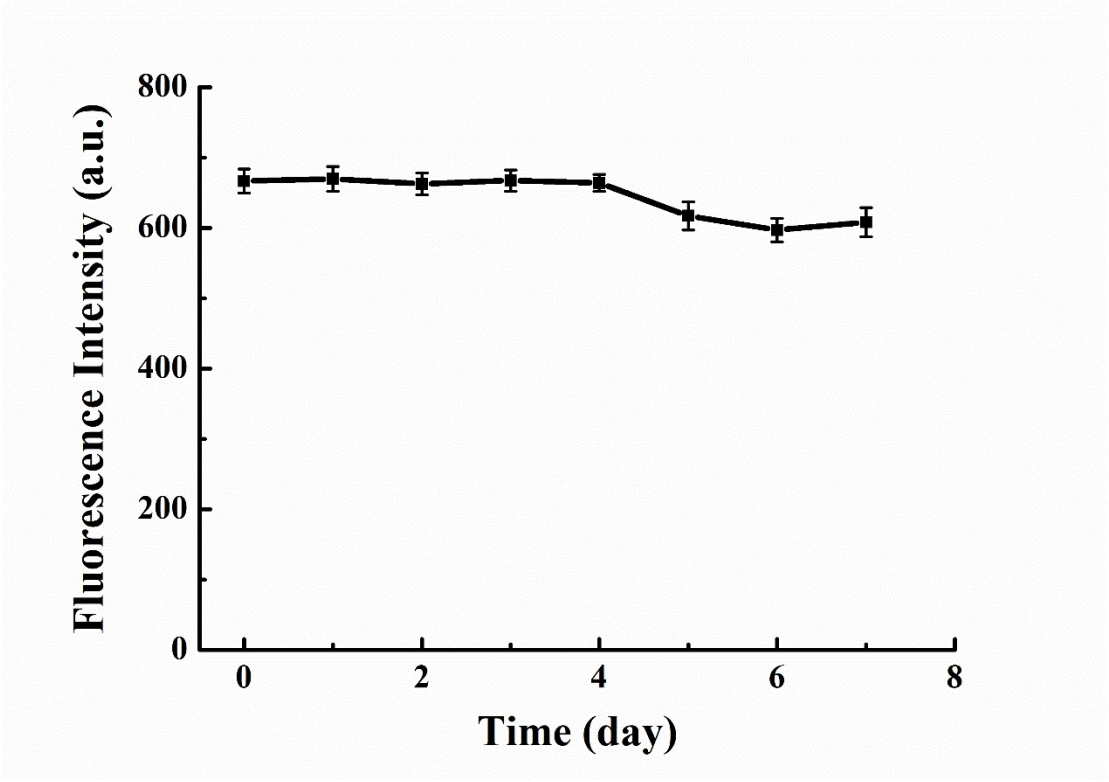

Fig. S2. Stability of the MSN-AuNCs. [MSN-AuNCs] = 0.4 mg/mL. (Ex=365 nm, Em = 570 nm)

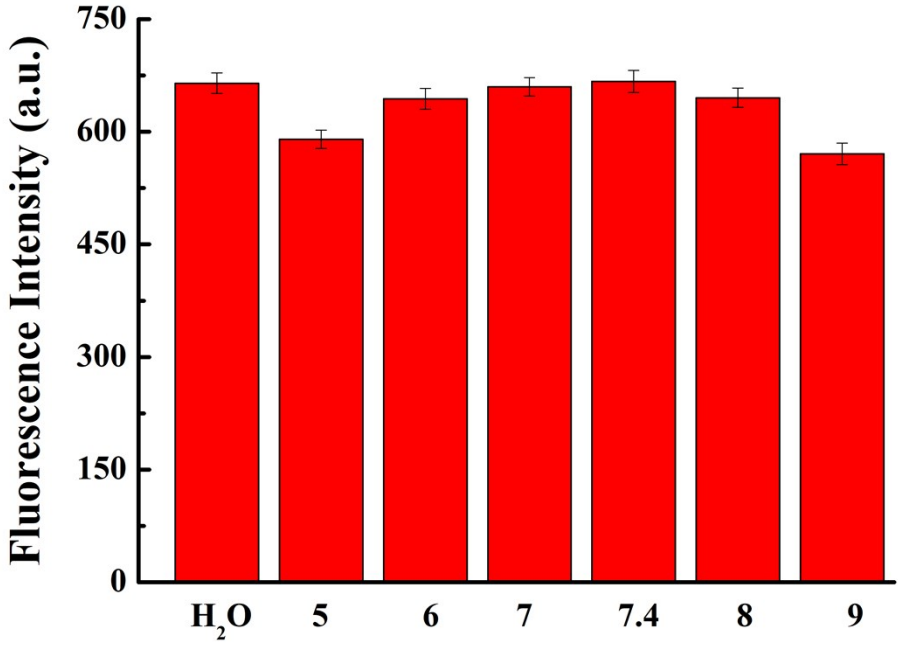

Fig. S3. Effect of pH on fluorescence intensity of MSN-AuNCs. [MSN-AuNCs] = 0.4 mg/mL. Buffer (10 mM Tris–HCl).

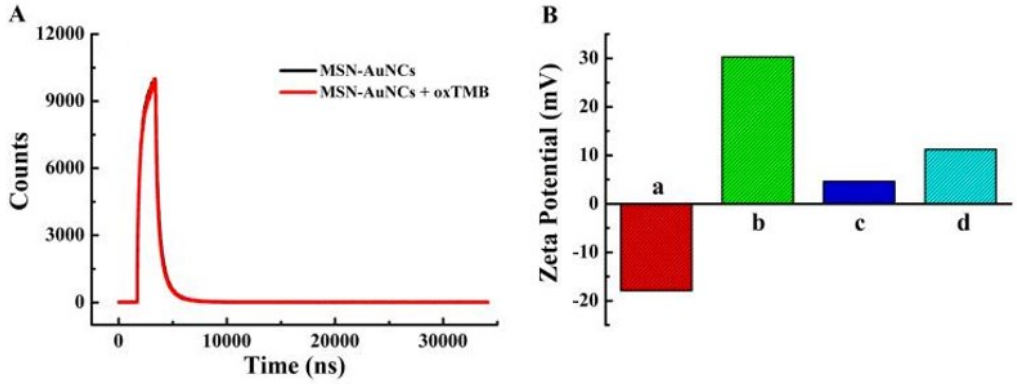

Fig. S4. (A) Fluorescence decay of the MSN-AuNCs as a function of time in the absence and presence of oxTMB. (B) Zeta potentials of (a) AuNCs, (b) MSNs, (c) MSN-AuNCs, (d) oxTMB.

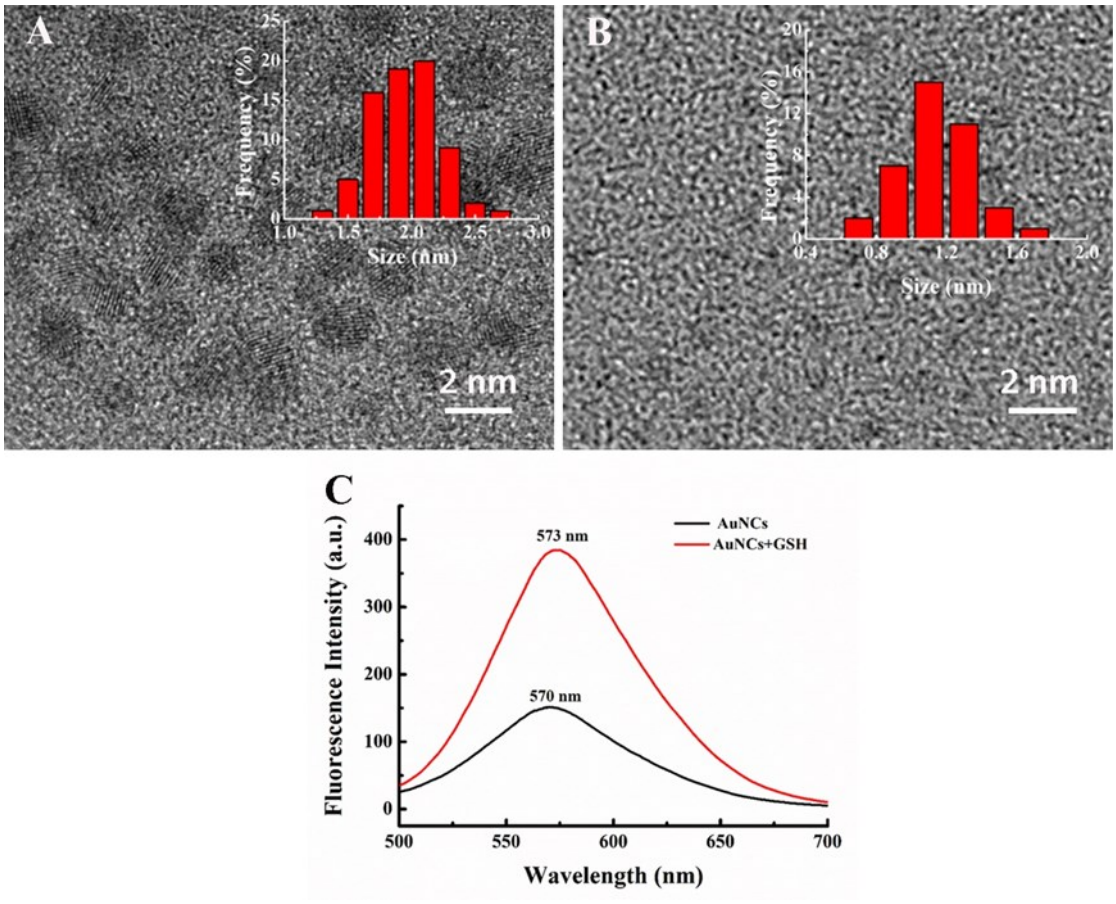

Fig. S5. TEM images of AuNCs in the absence (A) and presence (B) of GSH. (C) The corresponding fluorescence emission spectra of AuNCs in the absence and presence of GSH. [GSH] = 1 mM, Ex = 365 nm.

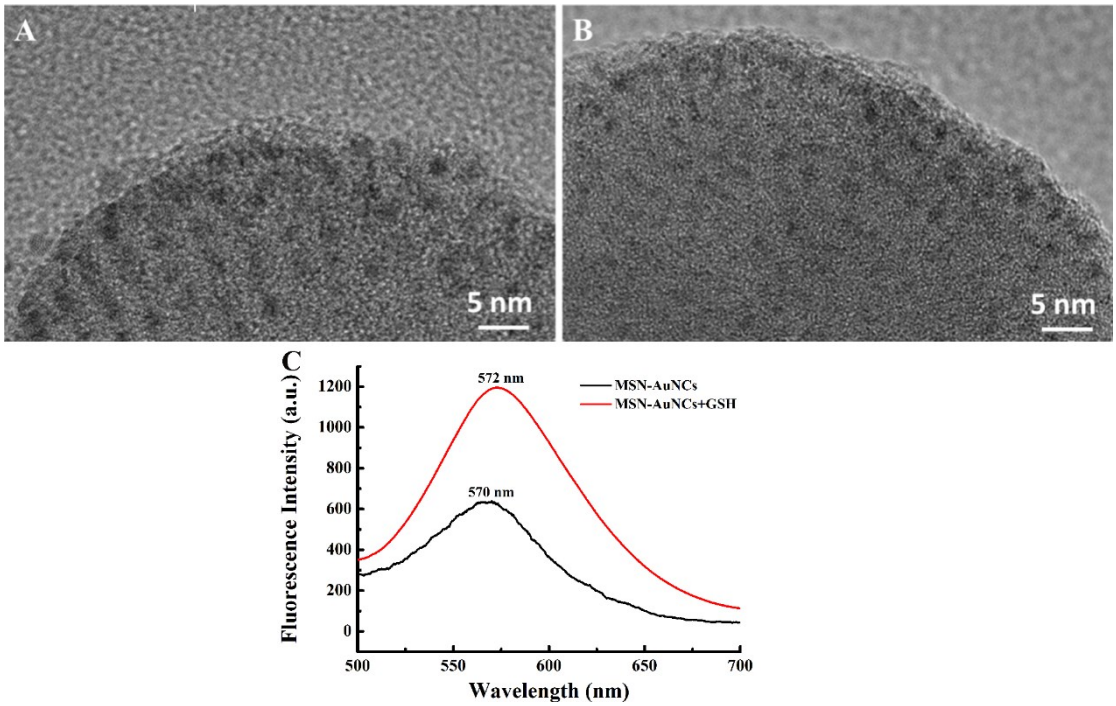

Fig. S6. TEM images of MSN-AuNCs sensing system in the absence (A) and presence (B) of GSH. (C) The corresponding fluorescence emission spectra of MSN-AuNCs and MSN-AuNCs in the absence and presence of GSH. [MSN-AuNCs] = 0.4 mg/mL, [GSH] = 1 mM, Ex = 365 nm.

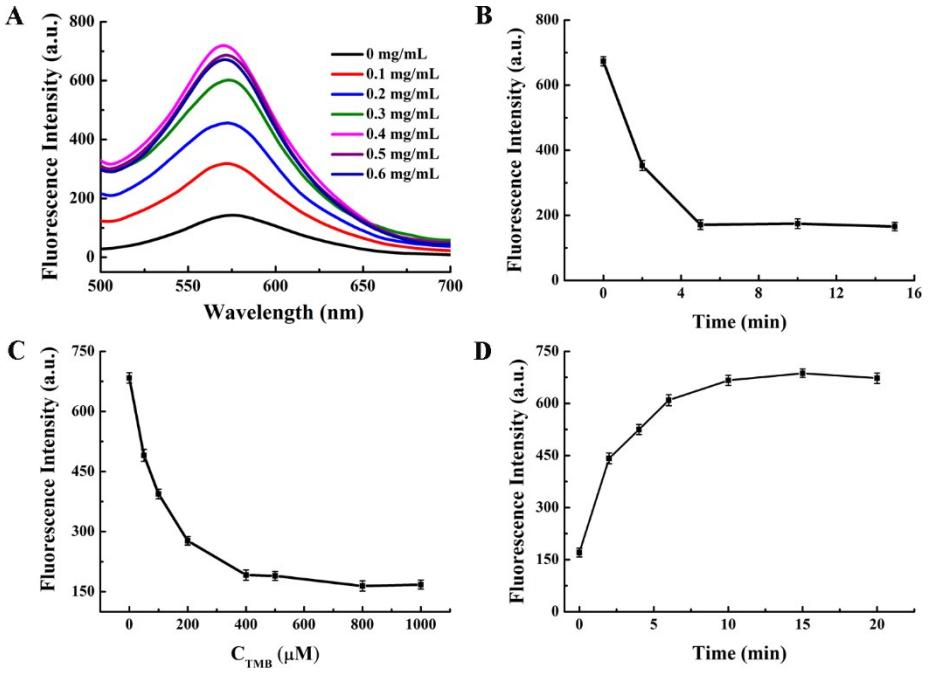

Fig. S7. (A) The effect of the concentration of MSNs on the fluorescence of MSN-AuNCs. (B) The effect of the incubation time of oxTMB on the fluorescence quenching of MSN-AuNCs. [TMB] = 800 μM, [MSN-AuNCs] = 0.4 mg/mL. (C) The effect of the concentration of TMB on the fluorescence of MSN-AuNCs. [MSN-AuNCs] = 0.4 mg/mL. (D) The effect of the incubation time of GSH for reduction of oxTMB on the fluorescence of MSN-AuNCs. [TMB] = 800 μM, [MSN-AuNCs] = 0.4 mg/mL, [GSH] = 100 μM. The error bars were estimated from three replicate measurements.

Table S1 Comparison of various methods for the determination of GSH.

Probe	Linear range (μM)	Detection limit (μM)	Mode	Ref.
Carbon dots- MnO_2	1-200	0.6	Fluorescence	3
AuNC@BSA-MnO_2	0-500	20	Fluorescence	4
Au(Ⅲ)/CDC [a]	0-150	2.02	Fluorescence	5
Au-AgNCs-$S_2O_8^{2-}$	1-100	0.2	Fluorescence	6
Polydopamine nanoparticles- MnO_2	0-350	1.5	Fluorescence	7
(N/S CDs)[b] -H_2O_2-TMB	0.20-100	0.26	Colorimetric	8
Fe_3O_4 NPs	3-30	3	Colorimetric	9
Nitrogen-functionalized carbon-TMB	0.05-15	0.5	Colorimetric	10
FeS_2 NPs-TMB-H_2O_2	0.2-35	0.15	Colorimetric	11
oxTMB/MSN-AuNCs	1-50,50-1000/1-30,30-1000	0.12/0.34	Fluorescence / Colorimetric	This work

[a] Au(Ⅲ) decorated carbon dots cluster

[b] Nitrogen and sulfur

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