## **Supporting Information**

## Co<sub>3</sub>O<sub>4</sub> nanocrystals as an efficient catalase mimic for colorimetric detection of glutathione

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Fig. S1. XRD patterns  $Co_3O_4$  nanocrystals.



Fig. S2. XPS spectra of the obtained  $Co_3O_4$  nanocrystals. (a) Survey XPS spectrum (b) High-resolution Co 2p spectrum. (c) High-resolution O 1s spectrum.



Fig. S3. FTIR spectrum for Co<sub>3</sub>O<sub>4</sub> nanocrystals.



Fig. S4. UV-vis spectra at reaction time of 5 min in different systems, inset is the photograph of the solution at a reaction time of 5 min in different reaction systems. From left to right: TMB  $+H_2O_2$ , TMB  $+Co_3O_4$  nanocrystals and TMB  $+H_2O_2 + Co_3O_4$  nanocrystals in a pH 5.0 acetate buffer at 25 °C.



Fig. S5. Effect of pH on catalytic activity of the  $Co_3O_4$  nanocrystals. Assay conditions: 0.5 mM TMB, 5 mM  $H_2O_2$ , 20 µg/mL  $Co_3O_4$  nanocrystals, 5 min.



Fig. S6. Dependence of catalytic activity on temperature. Assay conditions: 0.5 mM TMB, 5 mM  $H_2O_2$ , 20 µg/mL  $Co_3O_4$  nanocrystals, 5 min.



**Fig. S7.** Stablity of the  $Co_3O_4$  nanocrystals in two months. Assay conditions: 0.5 mM TMB, 5 mM  $H_2O_2$ , pH 5.0, 5 min. Inset: photograph of 20 µg/mL  $Co_3O_4$  nanocrystals (a) freshly prepared, (b) after two months



Fig. S8. Time-dependent absorbance changes at 652 nm in the presence of (1)  $Co_3O_4$  nanocrystals or (2) commercial 30 nm  $Co_3O_4$  nanoparticle. Assay conditions: 0.5 mM TMB, 5 mM H<sub>2</sub>O<sub>2</sub>, 20  $\mu$ g/mL catalyst, pH 5.0.



Fig. S9. Effect of the amount of  $Co_3O_4$  nanocrystals. Assay conditions: 0.5 mM TMB, 5 mM  $H_2O_2$ , pH 5.0, 5 min.



**Fig. S10.** Steady-state kinetics measurements of the  $Co_3O_4$  nanocrystals. (a) The concentration of  $H_2O_2$  was 5 mM and the TMB concentration varied. (b) The concentration of TMB was 0.5 mM and the  $H_2O_2$  concentration varied. Assay conditions: pH 5.0, 20 µg/mL  $Co_3O_4$  nanocrystals.



Fig. S11. Effects of  $Co_3O_4$  nanocrystals on the changes of 'OH with terephthalic acid as the fluorescence probe. Assay conditions: 5  $\mu$ M terephthalic acid, 5 mM H<sub>2</sub>O<sub>2</sub>, 0-30  $\mu$ g/mL Co<sub>3</sub>O<sub>4</sub> nanocrystals, pH 5.0, 5 min.



Fig. S12. Effects of  $Co_3O_4$  nanocrystals on the changes of  $O_2^-$  with dihydroethidium as the fluorescence probe. Assay conditions: 5  $\mu$ M terephthalic acid, 1 mM X, 1 U/mL XO, 0.1 mM DTPA, 30  $\mu$ g/mL  $Co_3O_4$  nanocrystals.



**Fig. S13.** UV-vis spectrum of Cyt *c*, Cyt *c* reacted with  $Co_3O_4$  nanocrystals and Cyt *c* reacted with  $Co_3O_4$  nanocrystals under deoxygenated condition.



**Fig. S14.** UV-vis spectrum of oxTMB (line 1) which was obtained by UV irradiation of a mixed solution of TMB and  $H_2O_2$  and oxTMB reacted with 40  $\mu$ M GSH (line 2) for 5 minutes.



**Fig. S15.** UV-vis spectrum of  $Co_3O_4$ -H<sub>2</sub>O<sub>2</sub>-TMB system (line 1),  $Co_3O_4$ -H<sub>2</sub>O<sub>2</sub>-TMB system upon the addition of 40  $\mu$ M GSH (line 2) and  $Co_3O_4$ (GSH pretreated)-H<sub>2</sub>O<sub>2</sub>-TMB system upon the addition of 40  $\mu$ M GSH (line 3).



Fig. S16. High-resolution Co 2p spectrum of GSH pretreated Co<sub>3</sub>O<sub>4</sub> nanocrystals



Fig. S17. GSH detection in serum sample. Assay conditions: 5  $\mu$ M terephthalic acid, 5 mM H<sub>2</sub>O<sub>2</sub>, 20  $\mu$ g/mL Co<sub>3</sub>O<sub>4</sub> nanocrystals, pH 5.0, 5 min. Serum was diluted for 1000 times.

Table S1. Comparison of the Michaelis-Menten constant (Km) and maximum reaction rate (Vm).

	Km (mM)		Vm (M s <sup>-1</sup> )		_
catalyst	TMB	$H_2O_2$	TMB	$H_2O_2$	ref
HRP	0.434	3.70	10×10-8	8.71×10 <sup>-8</sup>	7, 17
Co <sub>3</sub> O <sub>4</sub> nanocrystals	0.49	1.90	16×10 <sup>-8</sup>	12.7×10 <sup>-8</sup>	This work