Supplementary information

Redox Reaction Induced Ratiometric Fluorescence Platform for the Specific Detection of Ascorbic Acid Based on Ag_2S Quantum Dots and Multifunctional CoOOH Nanoflakes

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Contents

S1: Synthesis of CoOOH

The CoOOH was obtained by mixing 1.5 mL NaOH solution (1.0 M) with 50 mL $CoCl_2$ solution (10 mM), ultrasonic treatment for 5 min, centrifugation at 4000 rpm/min for 20 min, and then dispersed in 50 mL Milli-Q water. After that, 3 mL NaClO was added and an ultrasound was performed for 20 min. The obtained CoOOH NFs solution was centrifuged at 12000 rpm/min for 10 min and washed with water three times. Finally, the solution was dispersed in 50 mL Milli-Q water.

S2: The kinetic of the OXD-like activity

Various concentrations of TMB were added into acetate buffer with a fixed concentration of CoOOH NFs. When studying the Michaelis-Menten curves of TMB with different concentrations, the absorbance at 650 nm was measured. The V_{max} and K_m values were calculated using the Michaelis equation: $V = V_{max} [S]/(K_m + [S])$. Here, V_{max}, K_m, V, and [S] represent the maximum reaction rate, the Michaelis Menten constant, the initial reaction rate, and the concentration of the substrate, respectively.

S3: Synthesis of Ag_2S QDs

In a typical procedure, 0.0191 g DPA and 0.0272 g $AgNO_3$ were added into 40 mL of Milli-Q water. After stirring for 20 min, the uniform mixture was heated in the microwave oven at low temperature for 10 min. The color of the solution changed from colorless to light yellow and then to reddish brown. The Ag_2S QDs was filtered by a 0.22 μm ultrafiltration membrane and stored at 4 °C for further use.

S4: Quantum yield measurements

The QY of the as-prepared Ag_2S QDs was obtained using quinine sulfate in 0.1 M H_2SO_4 aqueous solution as the standard (quantum yield is 0.54) [1]. The highly diluted samples with the absorbances less than 0.05 (highly diluted samples can minimize the second optical processes such as re-absorption and re-emission effects) at the excitation wavelength were recorded, respectively. And the integrated fluorescence intensity was plotted against absorbance at the excitation wavelength and fitted into a linear function to obtain the slope. According to the two slopes (one obtained from the standard is called k_{std} and the other from the sample is called k_{sample}), the QY of Ag_2S QDs was calculated as 0.5% from eq. (2)[2]:

$$\Phi_{sample} = \frac{k_{sample}}{k_{std}} \times \frac{\eta_{sample}^{2}}{\eta_{std}^{2}} \times \Phi_{std} \qquad (2)$$

where Φ_{std} is the QY of the standard, k_{sample} and k_{std} are the slopes determined by the curves of Ag_2S QDs and standard, respectively. η_{sample} and η_{std} are the refractive indices of the sample and reference standard.

Figure S1. The optimization and kinetics of OXD-like activity

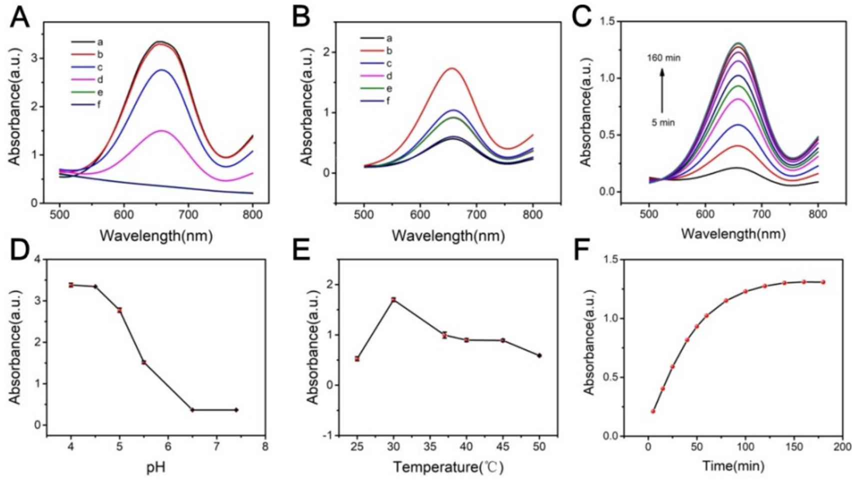

Figure S1. UV-vis absorption spectra of TMB + CoOOH NFs solution (A) at different pH of (a) 4.0, (b) 4.5, (c) 5.0 (d), 5.5, (e) 6.5 and (f) 7.4; (B) at different temperature (a) 25 ℃, (b) 30 ℃, (c) 37 ℃, (d) 40 ℃, (e) 45 ℃ and (f) 50 ℃. (C) at different time. Optimization the OXD activity of (D) pH, (E) temperature, (F) reaction time.

Figure S2. Fluorescence emission spectra of OPD, OPD + Co^{2+}, and OPD + CoOOH NFs.

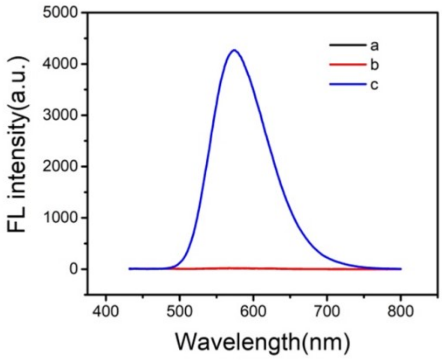

Figure S2. Fluorescence emission spectra of (a) OPD, (b) OPD + Co^{2+}, (c) OPD + CoOOH NFs.

Figure S3: Steady-state kinetic assay of Ag_2S-CoOOH.

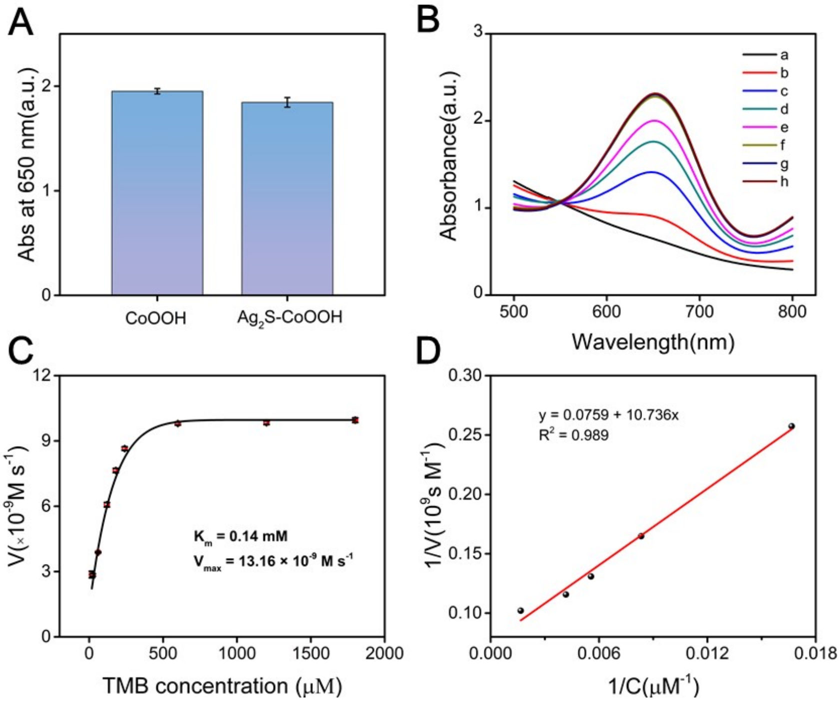

Figure S3. (A) The UV-vis absorbance of TMB treated with CoOOH and Ag_2S-CoOOH; (B) TMB + CoOOH NFs at different TMB concentrations: (a) 24 μM, (b) 60 μM, (c) 120 μM, (d) 180 μM, (e) 240 μM, (f) 0.6 mM, (g) 1.2 mM and (h) 1.8 mM; (C) Steady-state kinetic assay and oxidase-like activity catalytic mechanism at different TMB concentrations. Inset: The calculated K_m and V_{max} values; (D) Corresponding double reciprocal plots.

Figure S4: The mechanism study in detection of AA.

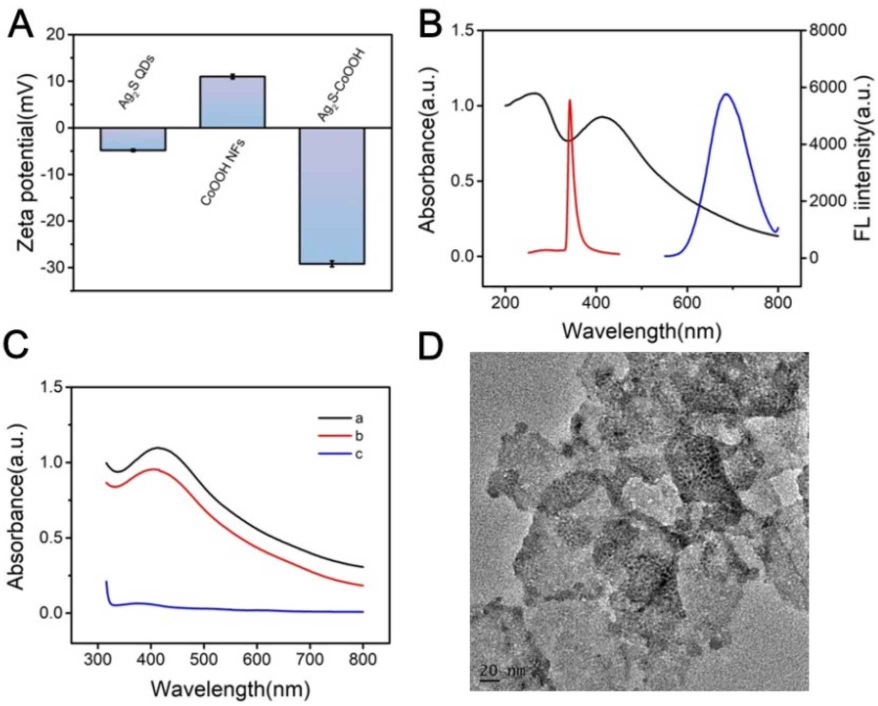

Figure S4. (A) Zeta potentials of Ag_2S QDs, CoOOH NSs and Ag_2S-CoOOH; (B) UV-vis absorption spectrum of CoOOH NFs (black curve) and fluorescence emission spectra (blue curve) and the excitation spectra (red curve) of Ag_2S QDs; (C) UV-vis absorption spectra of CoOOH nanoflakes (a), CoOOH + GSH (b) and CoOOH + AA (c). (D) TEM image of Ag_2S-CoOOH-GSH.

Figure S5: The influence of ionic strength toward Ag_2S-CoOOH.

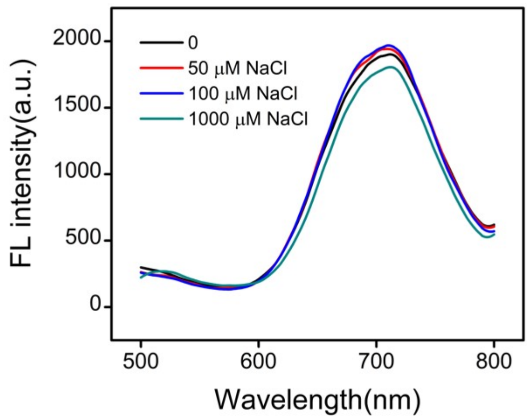

Figure S5. Fluorescence emission spectra of Ag_2S-CoOOH with the addition of different concentrations of NaCl.

Figure S6: The XPS spectra of Ag in Ag_2S-CoOOH and Ag_2S-CoOOH-AA.

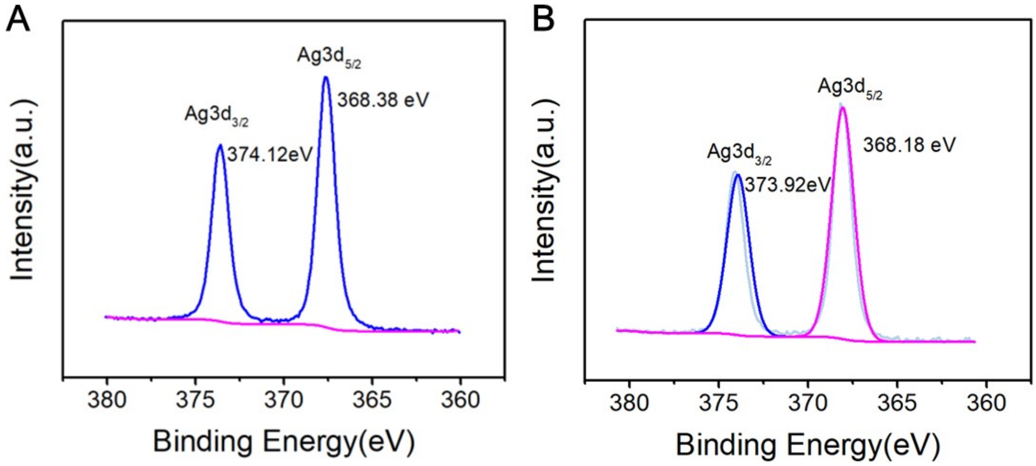

Figure S6. The corresponding XPS spectra of Ag in Ag_2S-CoOOH in the absence (A) and presence (B) of AA.

Figure S7. Optimization the detection of AA.

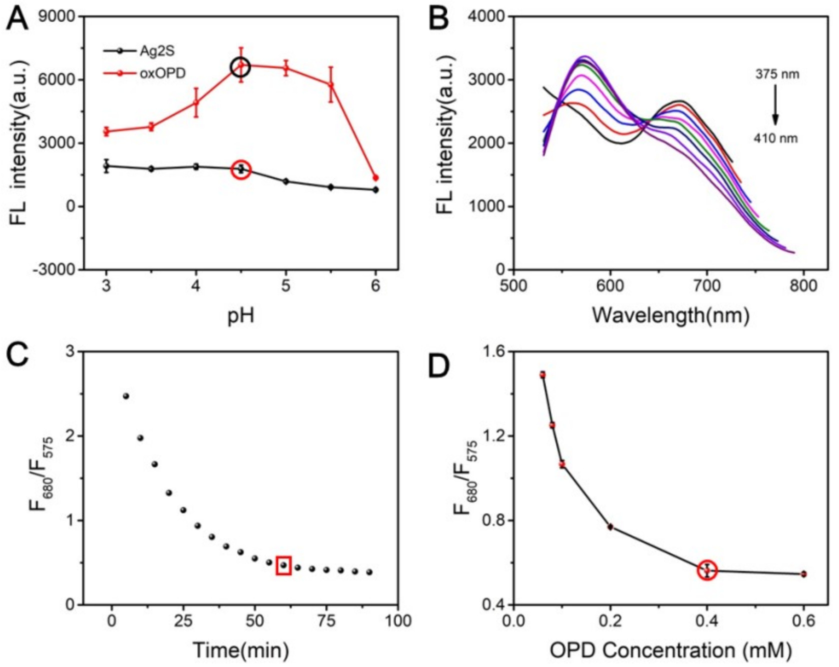

Figure S7. Fluorescence intensity of Ag_2S-CoOOH-OPD under different pH (A) and different excitation wavelengths (B); Ratiometric fluorescence change under different incubating time (C) and different concentration of OPD (D).

Table S1. Comparison of steady-state kinetic parameter of CoOOH and other nanozymes.

Catalyst	K_m (mM)	V_{max} (10^{-8} M s^{-1})	Ref
CeO_2 NPs	0.80	30	[3]
Co–Fe LDH	0.218	/	[4]
POM@CuO NPs	1.084	2.72	[5]
Pt NPs	0.63	/	[6]
CoOOH	0.1	0.198	This work

Table S2. Determination of the concentrations of AA in real samples.

Sample	Found (μM)	Added (μM)	Detected (μM)	Recovery (%)	RSD (%)
		10.0	12.1	98.0	4.3
lime juice	2.3	100.0	107.1	104.8	8.7
		1000.0	970.6	96.8	3.2
		10.0	12.2	111.7	6.4
human serum	0.9	100.0	115.6	113.9	5.2
		1000.0	993.6	99.2	3.7

Reference

1. G. Yin, Y. Gan, H. Jiang, T. Yu, M. Liu, Y. Zhang, H. Li, P. Yin and S. Yao, *Anal Chem*, 2021, **93**, 9878-9886.
2. H. El-Kashef, *Physica B: Condensed Matter*, 2000, **279**, 295-301.
3. A. Asati, S. Santra, C. Kaittanis, S. Nath and J. M. Perez, *Angew. Chem. Int. Ed. Engl*. 2009, **48**, 2308-2312.
4. J. Zhao, Y. Xie, W. Yuan, D. Li, S. Liu, B. Zheng and W. Hou, *J Mater. Chem. B* 2013, **1**, 1263-1269.
5. Y. Xu, P. Li, X. Hu, H. Chen, Y. Tang, Y. Zhu, X. Zhu, Y. Zhang, M. Liu and S. Yao, *ACS Appl. Nano Mater.* 2021, **4**, 8302-8313.
6. C. J. Yu, T. H. Chen, J. Y. Jiang and W. L. Tseng, *Nanoscale*, 2014, **6**, 9618-9624.