

Synthesis of Zn-MOF fluorescent material for sensitive detection of biothiols via internal filtration effect with MnO₂ nanosheets

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Experimental section

Chemicals and apparatus

N, N-dimethylformamide, L-glutathione (98%), cysteine, alanine (Ala), phenylalanine (Phe), threonine (Thr) and isoleucine (Leu) were purchased from Aladdin Reagent Corporation. Zinc nitrate hexahydrate was purchased from Xilong Scientific Co., Ltd. Benzophenone 4,4' -dicarboxylic acid (H₂BPDB) was purchased from Tixiai Chemical Industry Development Co., Ltd. (Shanghai, China). 4,4',4''-Nitrilotribenzoic acid (H₃NTB), glycine (Gly), aspartic acid (Asp), lysine (Lys), dopamine (DA), and glutamic acid (Glu) were purchased from Shanghai Maclin Biochemistry Co., Ltd. 30% hydrogen peroxide, tetramethylammonium hydroxide, manganous nitrate, and methyl alcohol were purchased from Sinopharm Group Chemical Reagent Co., Ltd. Manganese chloride was purchased from Sheng Gong Biological Engineering Co., Ltd. Tyrosine (Tyr) was purchased from Adamas-beta Reagent Co., Ltd. Arginine (Arg) was purchased from Sigma-Aldrich Corporation.

The composite was recorded with a GENESYS-150 UV-Vis absorption spectrometer. The aqueous solution of Zn-MOFs was characterized by a Lengguang F96pro fluorescence spectrophotometer under the conditions that the excitation wavelength was 355 nm and the measurement voltage was 650 V. The surface morphology and size of the Zn-MOFs were observed by QUANTA 450 environmental scanning electron microscopy (ESEM). The morphology of MnO₂ was observed using Tecnai G2 transmission electron microscopy (TEM). Powder XRD patterns were obtained using a MiniFlex600 powder X-ray diffractometer using Cu K_α radiation ($\lambda=1.540\text{\AA}$). Simultaneous thermogravimetric analysis (TGA) and thermogravimetry (Japan Rigaku Corporation) was used to determine Zn-MOFs. The zeta potential was measured on a ZetaLitesizer nanoparticle potentiometer. The fluorescence lifetime was collected using an Edinburgh FS5 spectrofluorometer. FTIR spectra were recorded on a Nicolet Avatar-330 spectrometer.

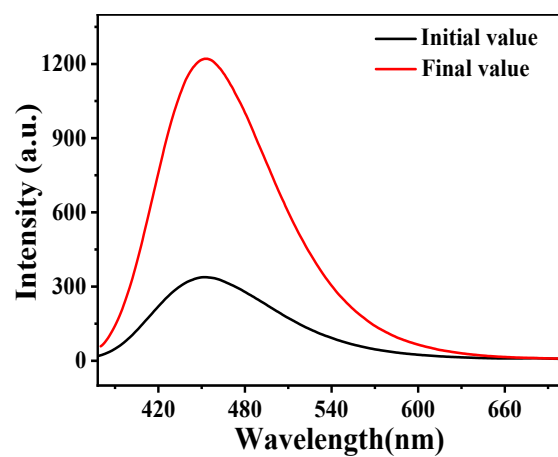


Fig. S1. The fluorescence intensity of Zn-MOF before and after optimizing the synthesis conditions

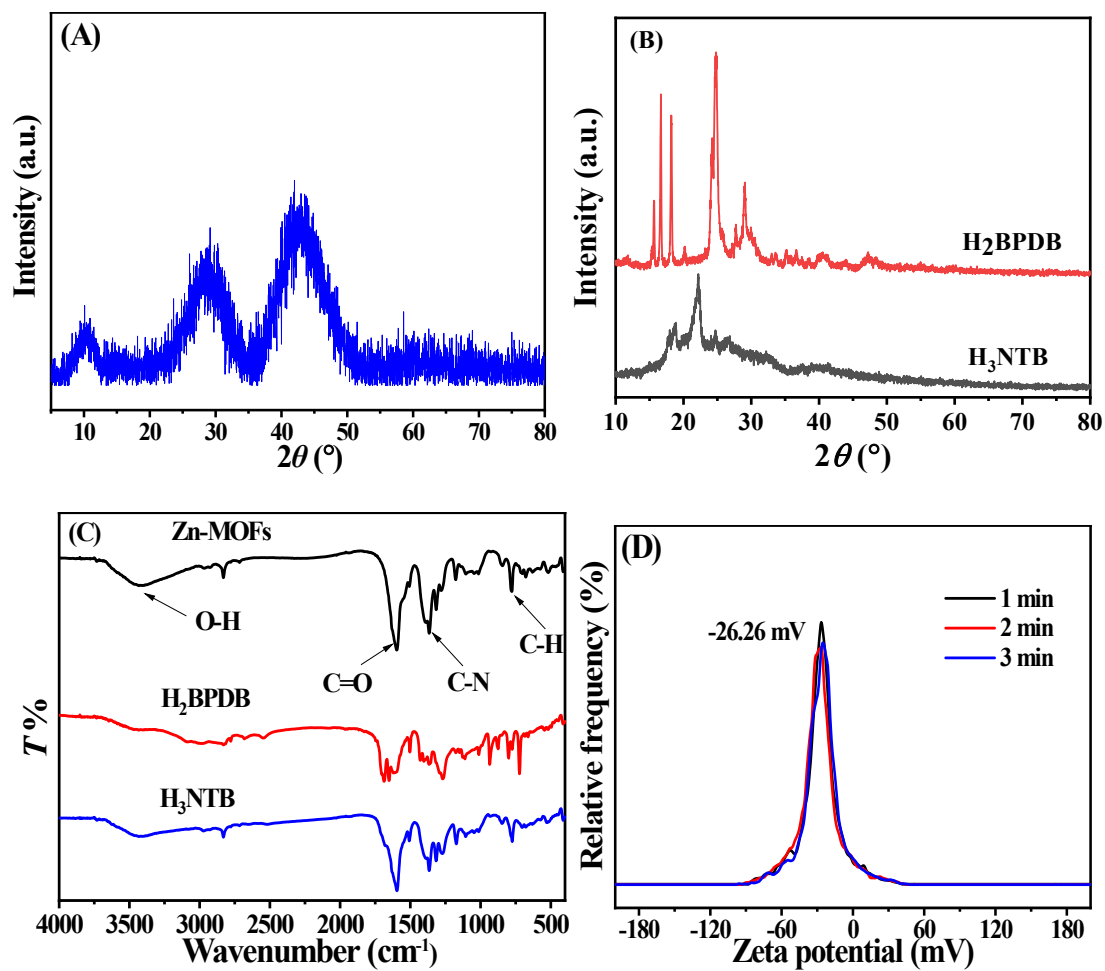


Fig. S2. XRD patterns of (A) Zn-MOFs and (B) the two ligands, (C) FTIR of different samples, (D) zeta potential of Zn-MOFs

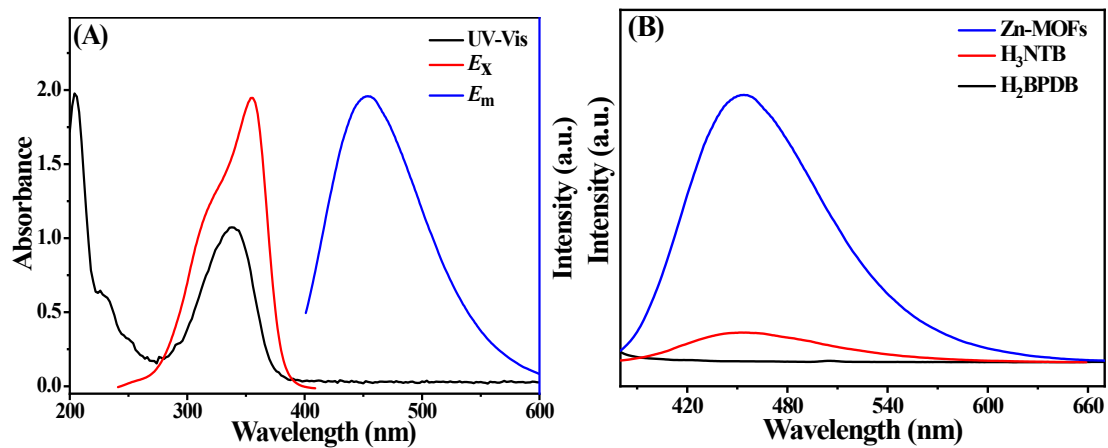


Fig. S3. (A) UV-Vis absorption and fluorescence spectra of Zn-MOFs, (B) fluorescence of Zn-MOFs and organic ligands of Zn-MOFs aqueous solution

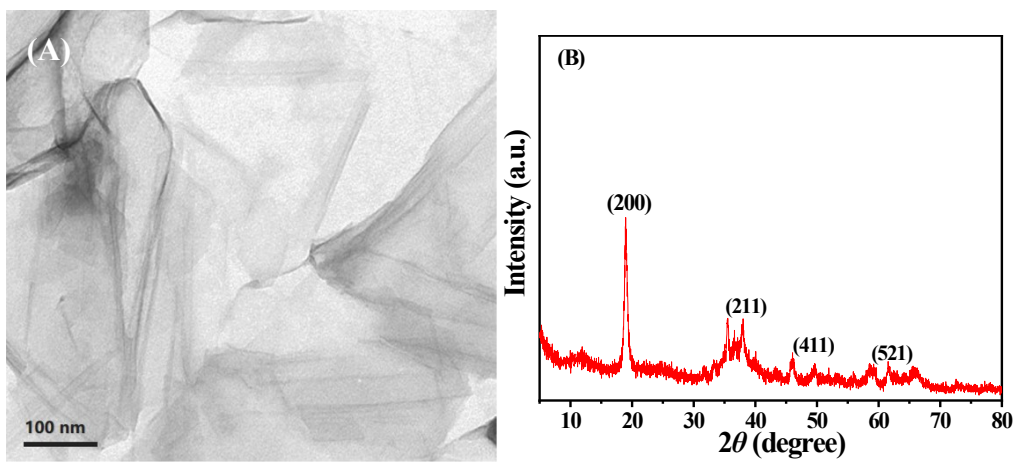


Fig. S4. (A) TEM image and (B) XRD pattern of MnO₂ NSs

Table S1 Comparison of different GSH detection methods based on MnO₂ as an intermediate

Materials	Detection method	Linear range	LOD	Refs.
BNQDs	Fluorescence	0.50 μ M ~ 0.25 mM	160 nM	1
COFs	Fluorescence	0.50 μ M ~ 0.10 mM	280 nM	2
WS ₂ QDs	Fluorescence	0.00 μ M ~ 0.06 mM	120 nM	3
de-CDs	Fluorescence	1.00 μ M ~ 10.00 mM	600 nM	4
Au	Fluorescence	0.50 μ M ~ 0.03 mM	100 nM	5
MnO ₂ /PS	Colorimetry	1.00 μ M ~ 0.05 mM	80 nM	6
Ag	Colorimetry	0.10 μ M ~ 55.00 μ M	80 nM	7
Zn-MOFs	Fluorescence	0.00 μ M ~ 0.16 mM	67 nM	This work

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