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Supplementary Information for

Phosphorescence detection of 2-Mercaptobenzothiazole in Environmental water samples by Mn-doped ZnS quantum dots

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Materials and methods

Reagents and chemicals

All chemicals used were of analytical reagent grade. Mercaptopropionic acid (MPA), $ZnSO_4·7H_2O$, $MnCl_2$ were procured from Tianjin Kermel Chemical Reagent Co. Ltd (Tianjin, China). $Na_2S·9H_2O$, NaH_2PO_4, Na_2HPO_4 were purchased from Tianjin Guangfu Chemical Reagents Co. Ltd (Tianjin, China). 2-Mercaptobenzothiazole (MBT) were available from Aladin Reagents Co. Ltd (Shanghai, China). All the solutions were prepared in Milli-Q water with a resistivity of 18.2 $MΩ.cm^{-1}$, which produced from a Water Pro water purification system (Labconco Corporation, Kansas City).

Instrumentation

Phosphorescence spectroscopy measurements were performed by a Cary Eclipse spectrophotometer in the wavelength range of 450-750 nm upon excitation at 295 nm (Varian, American), equipped with a plotter unit and a quartz cell (1.0 cm×1.0 cm) in the phosphorescence mode. The slit widths were 10 and 10 nm for excitation (295 nm) and emission (590 nm), respectively. UV-visible absorption spectra were performed on a Cary 300 UV-visible spectrophotometer (Varian, American). The size and morphology of QDs were characterized by a JSM-2100(JEOL, Japan) transmission electron microscope (TEM) . The samples for TEM were obtained by drying sample droplets from water dispersion onto a 100-mesh Cu grid coated with a lacey carbon film, which was then allowed to dry prior to imaging. The microstructure of QDs were characterized by a D8 Advance (Bruker, Germany) X-ray diffractometer (Cu K_{α}).

Preparation of aqueous MPA - caped Mn-doped ZnS quantum dots

Mn-doped ZnS QDs were successfully prepared in an aqueous solution using MPA as a stabilizer, as reported in the previous report.[1] In brief, 50 mL of 0.04 M MPA, 5 mL of 0.1 M $ZnSO_4$, and 2 mL of 0.01 M $MnCl_2$ were added to a three-necked flask. The mixture was adjusted to pH 11 with 1 M NaOH and stirred under nitrogen at room temperature for 30 min. Then 5 mL of 0.1 M Na_2S was quickly injected into the solution with deoxygenated to allow the nucleation of the nanoparticles. After stirring for 20 min, the solution was aged at 50℃ under open air for 2 h to form MPA-capped Mn-doped ZnS QDs. These QDs were obtained after being precipitated with the same volume of ethanol, separated by centrifuging with 4000 rpm for 10 min, and dried in vacuum. The prepared QDs powder is highly soluble for further experiments.

Phosphorescence experiments

A stock solution of MBT (0.2 $mg.mL^{-1}$) was prepared in ethanol solution and MBT with various concentrations were obtained by serial dilution of the stock solution. For the detection of MBT, 100 μL of 2.0 $mg.mL^{-1}$ MPA-capped Mn-doped ZnS QDs, 250 μL of 0.2 M PBS buffer solution (pH 9.0) were sequentially added to a 10 mL calibrated test tube, MBT standard solution or the real sample was added to the mixture solution, and then diluted to 5.0 mL with ultrapure water. The solution was mixed thoroughly and equilibrated for 10 min to measure the phosphorescence intensity at the excitation wavelength of 295 nm.

Sample Collection and Pretreatment.

Water samples were collected from three main sources: (1) Fen river passing through Linfen City. (2) Lake water from a small lake in Shanxi Normal University (Linfen, Shanxi, China). (3) Tap water from our laboratory. All the samples were centrifuged at 4 000 rpm for 10 min to remove suspended Solids, and supernatant was filtered through a 0.22 μm water phase membrane. All of the sample solutions were kept at 4℃ and analyzed within 2 days. After suitable dilution (1:10,v/v), the samples were introduced to the phosphorescence system.

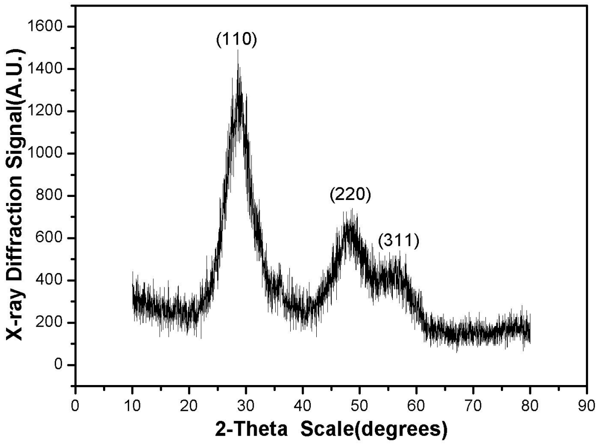

Fig. S1 XRD pattern of MPA-capped Mn-doped ZnS QDs.

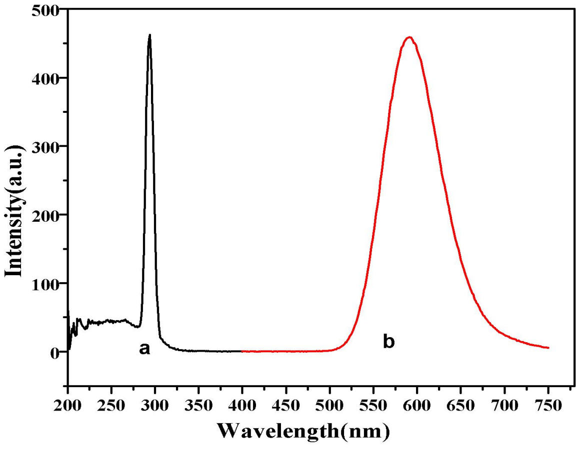

Fig. S2 Phosphorescence excitation and emission spectra of MPA-capped Mn-doped ZnS QDs (40 μg mL^{-1}). Solutions were prepared in PBS buffer (pH 9.0, 0.01M).

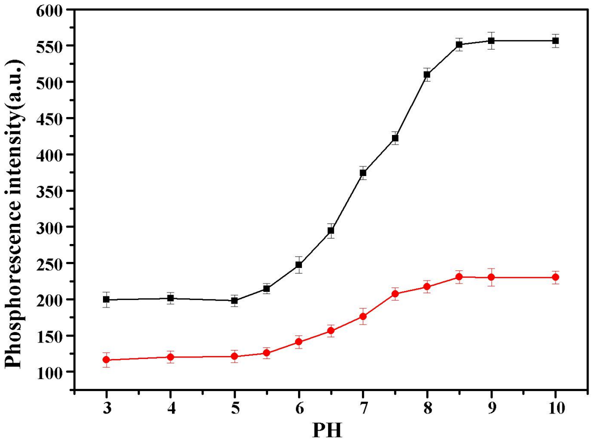

Fig. S3 Effect of pH on phosphorescence intensity of (a) MPA-capped Mn-doped ZnS QDs and (b) quenched phosphorescence intensity of MPA-capped Mn-doped ZnS QDs in the presence of 8 μg mL^{-1} MBT (the red line). all solutions were prepared in 0.01mol·L^{-1} of phosphate-buffered saline buffer at pH 3.0, 4.0, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5 8.0, 8.5, 9.0, and 10.0.

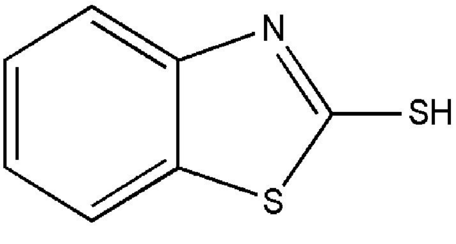

Fig. S4 Molecular structure of 2- mercaptobenzothiazole (MBT).

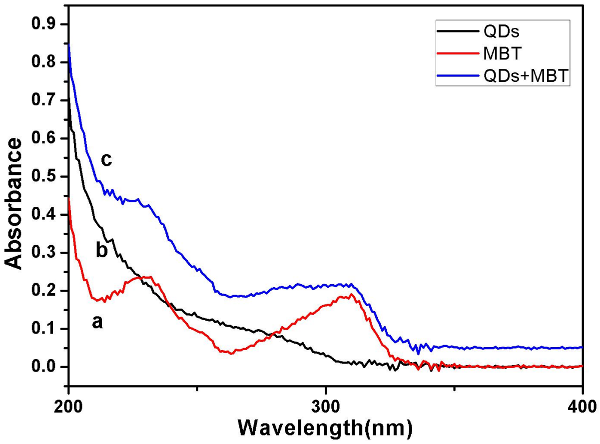

Fig. S5 UV/Vis absorption spectra of (a) MBT, (b) MPA-capped Mn-doped ZnS QDs, (c) MPA-capped Mn-doped ZnS QDs+MBT, the concentration of MBT and MPA-capped Mn-doped ZnS QDs are 2 μg.mL^{-1} and 10 μg.mL^{-1}, respectively.

Table S1 Comparison of the proposed method with different analytical techniques reported for determination of MBT

Methods	Linear range(μg.mL^{-1})	Detect limit (μg.mL^{-1})	Ref.
SWV	7.0-40.0	0.14	[12]
UV-HPLC	10.0-120.0	2.80	[40]
Electrochemical	0.1672-602.1	0.08	[15]
GC-MS	0.02007-0.02509	0.020	[41]
RTP	0.10-12.0	0.075	this work

Table S2 Analytical results for the determination of MBT in real samples

Samples	Found without Spiking(μg.mL^{-1})	Spiked (μg.mL^{-1})	Found (μg.mL^{-1})	Recovery (%)	RSD (n=3,%)
River Water	Not detected	0.1	0.101±0.0022	101%	2.2
		0.2	0.193±0.0052	97%	2.7
Lake Water	Not detected	0.1	0.098±0.0028	98%	2.9
		0.2	0.194±0.0047	97%	2.4
Tap Water	Not detected	0.1	0.0990±0.0023	99%	2.3
		0.2	0.196±0.0045	98%	2.3

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