Formaldehyde sensing based on the catalytic reaction of β-HgS nanocrystals

Jiang-Shan Shen,* Jia-Jia Wu, Xiang-Ying Sun, Zhen-Long Wu, Ping Gao and Bin Liu

College of Materials Science and Engineering, Huaqiao University, Xiamen 361021, China. E-mail: jsshen@hqu.edu.cn

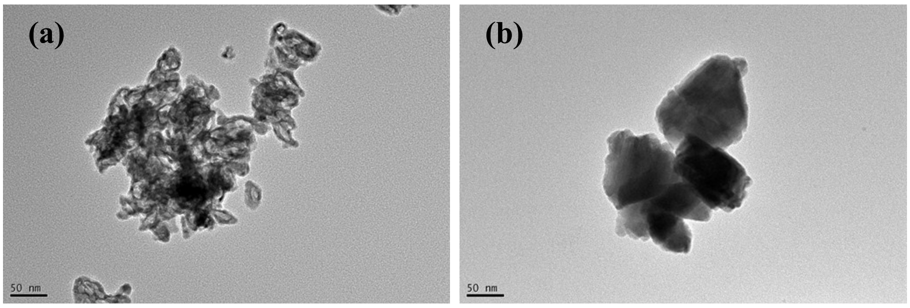

Fig. S1 TEM images of α (a)- and β (b)-HgS nanocrystals.

Fig. S2 Typical photographs of TMB solution in the irradiation of room light (a), and photographs of OPD solution illuminated by 365 nm UV lamp in dark (b) in the presence of a series of metal sulfide nanomaterials. Experimental conditions: (a) [TMB] = 0.5 mM; metal sulfide nanomaterials concentration was set to be 0.333 mg·mL^{-1}; reaction temperature of 37 ^{o}C; reaction time of 30 min. (b) [OPD] =0.25 mM; metal sulfide nanomaterials was set to be 0.125 mg·mL^{-1}; reaction temperature of 65 ^{o}C; reaction time of 60 min.

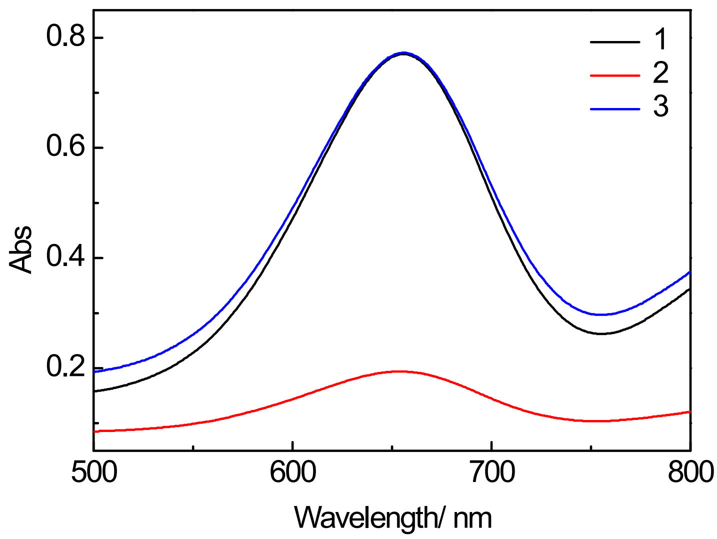

Fig. S3 The comparison of TMB-β-HgS nanocrystals solution in the presence (1) and absence (2) of dissolved oxygen, in the absence of room light (3). Experimental condition: [TMB] = 0.5 mM; β-HgS nanocrystals concentration was set to be 0.333 mg·mL^{-1}; reaction temperature of 37 ^{o}C; 0.2 M HOAc-NaOAc buffer solution of pH 4.2; reaction time of 30 min.

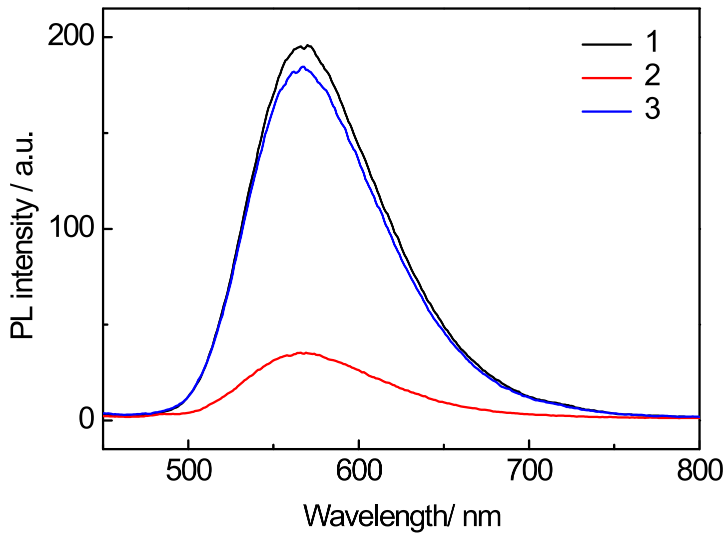

Fig. S4 The comparisons of OPD-β-HgS nanocrystals solution in the presence (1) and absence (2) of dissolved oxygen, in the absence of room light (3). Experimental conditions: [OPD] =0.25 mM; β-HgS nanocrystals concentration was set to be 0.125 mg·mL^{-1}; reaction temperature of 65 ^{o}C; 50 mM Tris-HCl buffer solution of pH 7.4; reaction time of 60 min.

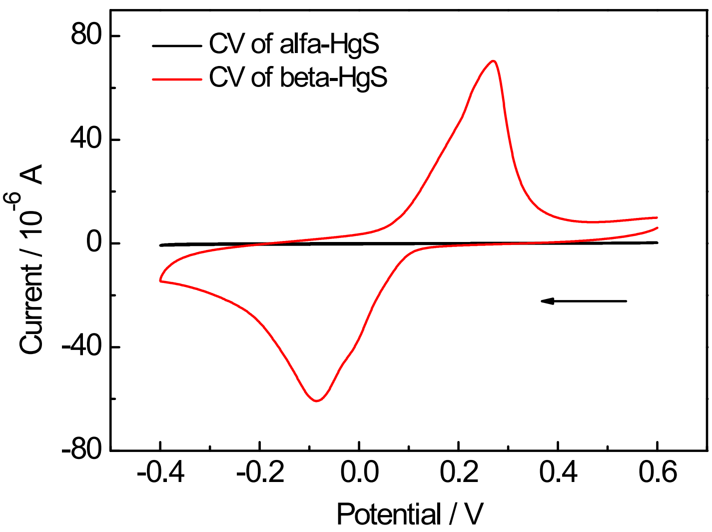

Fig. S5 CV curves of α -(black line) and β- (red line) HgS nanocrystals in N_2 -saturated 50 mM Tris-HCl solution of pH 7.4. Scanning rate was 30 mV. s^{-1}.

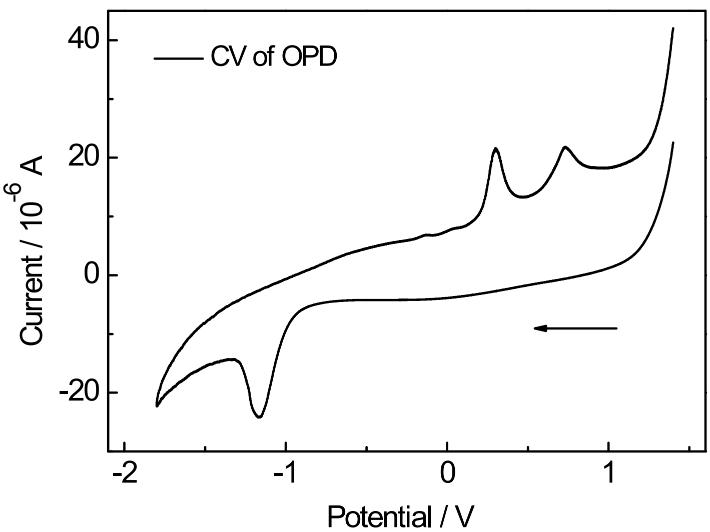

Fig. S6 CV curve of OPD in N_2 -saturated 50 mM Tris-HCl solution of pH 7.4. Scanning rate was 30 mV. s^{-1}.

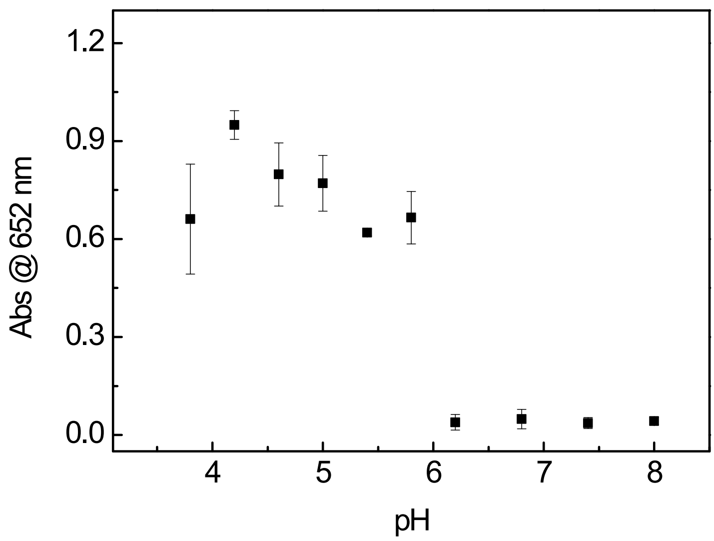

Fig. S7 pH-dependent oxidase-like activity of β-HgS nanocrystals towards TMB. Experimental conditions: [TMB] = 0.5 mM; β-HgS nanocrystals concentration was set to be 0.333 $mg \cdot mL^{-1}$; reaction temperature of 37 ^oC; reaction time of 30 min.

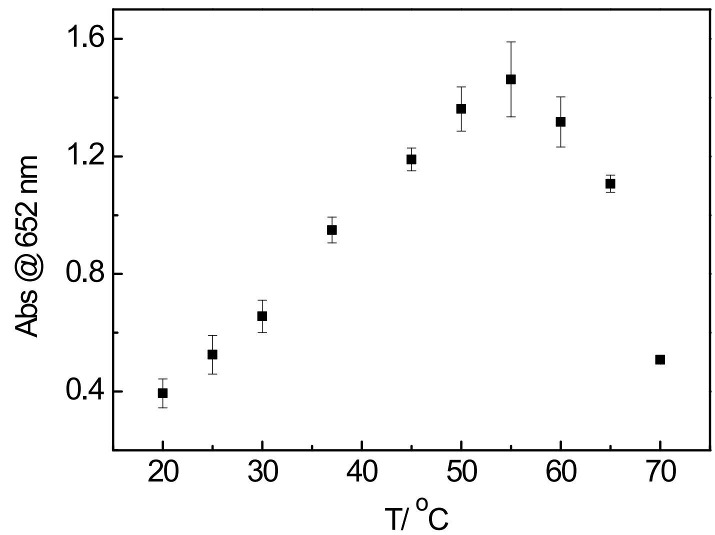

Fig. S8 Temperature-dependent oxidase-like activity of β-HgS nanocrystals towards TMB. Experimental conditions: [TMB] =0.5 mM; β-HgS nanocrystals concentration was set to be 0.333 $mg \cdot mL^{-1}$; 0.2 M NaOAc-HOAc buffer solution of pH 4.2; reaction time of 30 min.

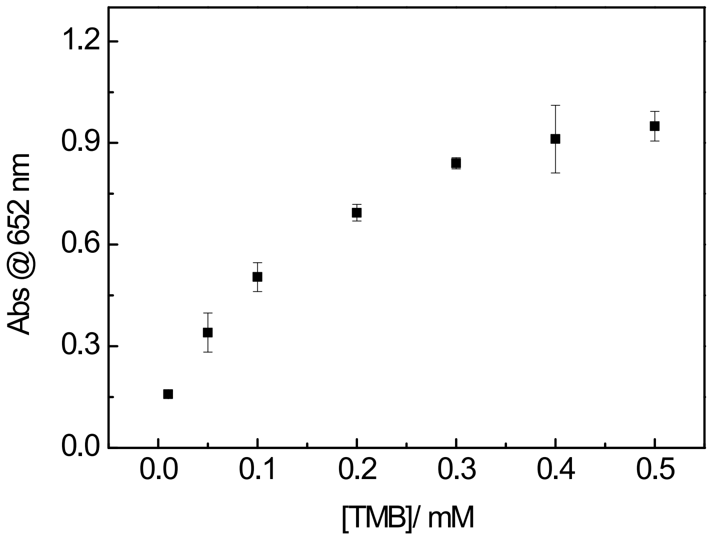

Fig. S9 The relationship between Abs @ 652 nm and TMB concentration. Experimental conditions: *β*-HgS nanocrystals concentration was set to be 0.333 mg·mL^{-1}; reaction temperature of 37^{o}C; 0.2 M NaOAc-HOAc buffer solution of pH 4.2; reaction time of 30 min.

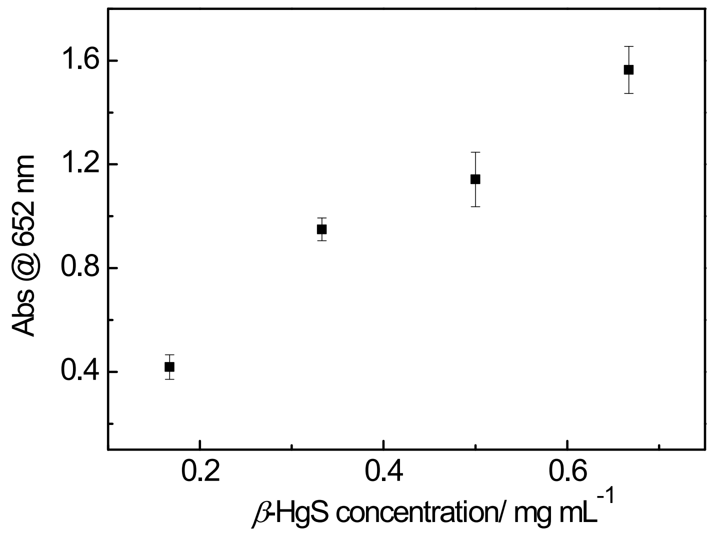

Fig. S10 The relationship between Abs @ 652 nm and *β*-HgS nanocrystals concentration. Experimental conditions: [TMB] = 0.5 mM; reaction temperature of 37 ^{o}C; 0.1 M NaOAc-HOAc buffer solution of pH 4.2; reaction time of 30 min.

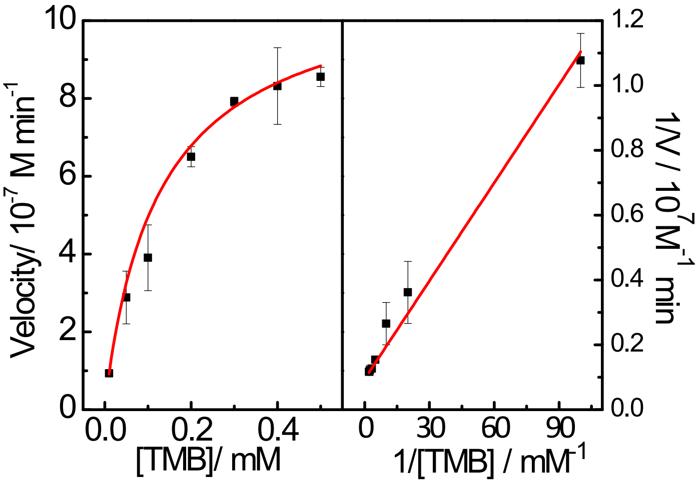

Fig. S11 Steady-state kinetic analysis of the oxidation reaction of TMB catalyzed by β-HgS nanocrystals on the basis of the Michaelis–Menten model.

Table S1 Kinetic parameters of the β-HgS nanocrystals –TMB system

[E](mg·mL^{-1})[a]	K_m (mM)	V_{max} (M min^{-1})	K_{cat} (min^{-1})
0.333	0.146	1.132×10^{-6}	7.92×10^{-4}

[a] β-HgS nanocrystals concentration of 0.333 mg·mL^{-1} was equalled to be1.43×10^{-3} M, referred to Hg molar concentration.

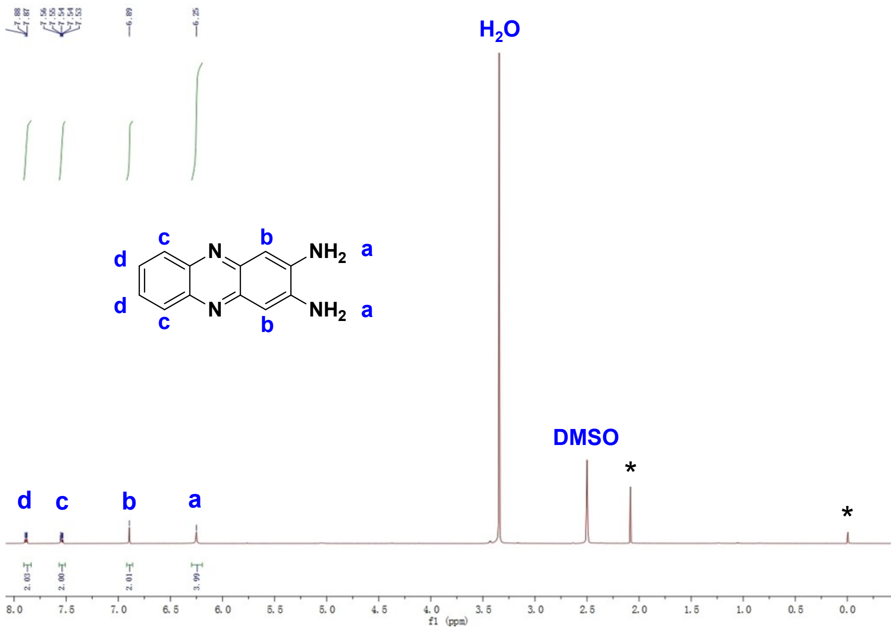

Fig. S12 ^{1}H NMR spectrum (500 MHz) of purified the oxidation product in DMSO-d_6 of OPD catalyzed by β-HgS nanocrystals. The marked "*" peaks are unknown peaks.

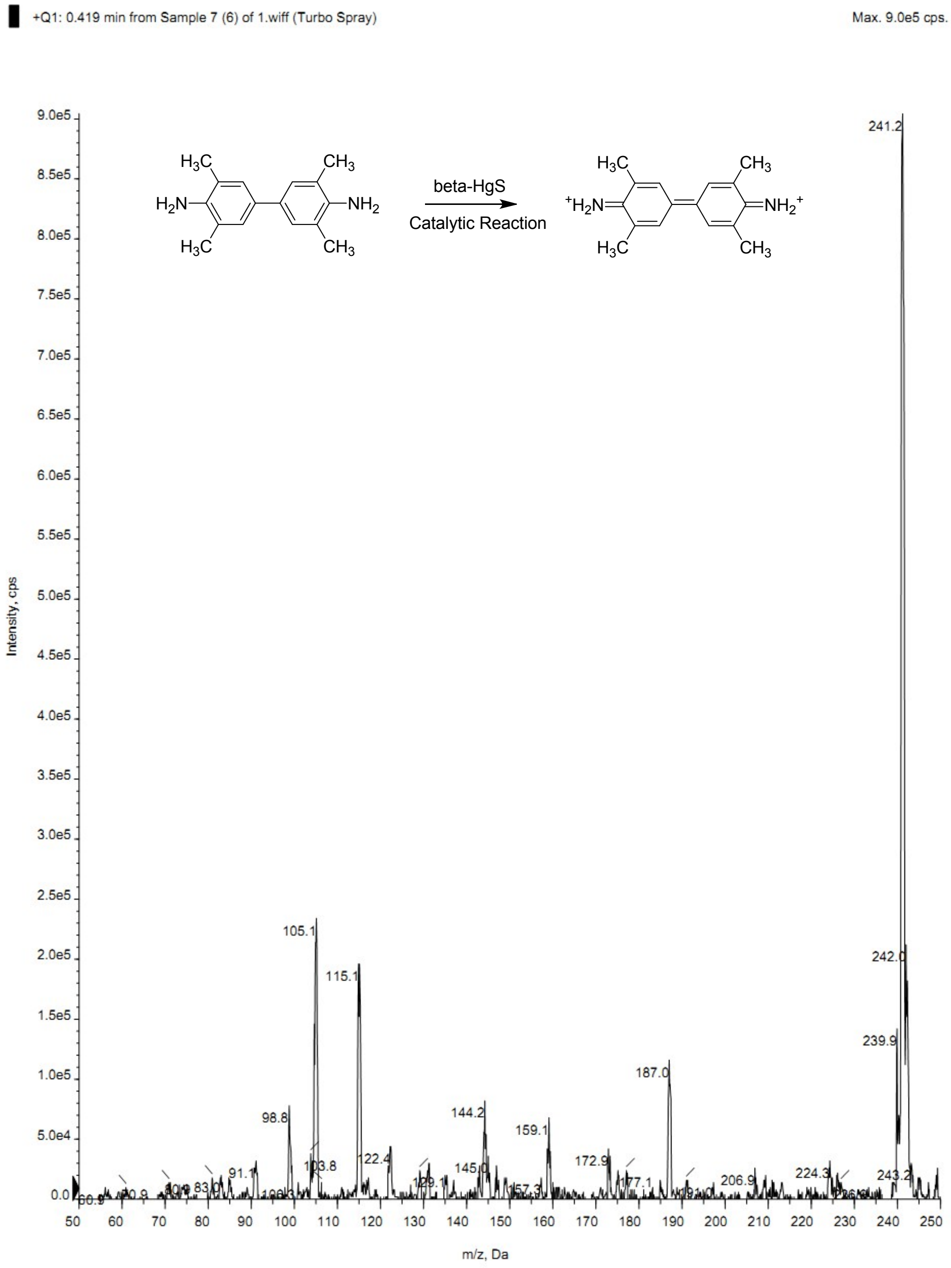

Fig. S13 The ESI-MS result of the extracted solution of the β-HgS nanocrystals- TMB catalytic reaction system by chloroform.

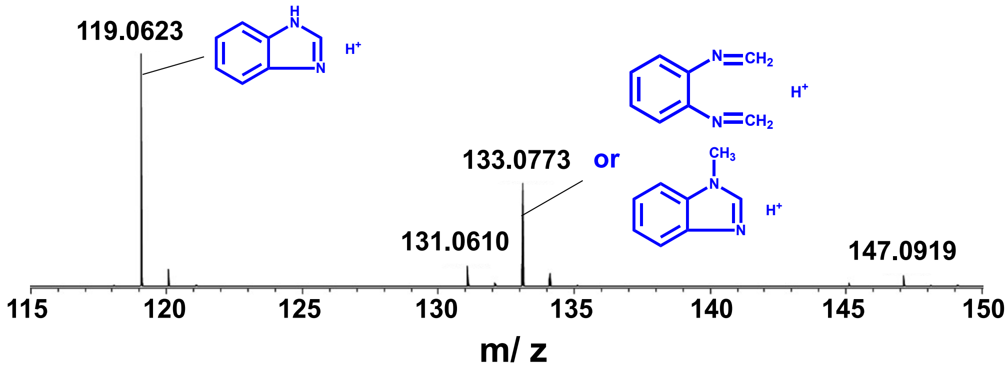

Fig. S14 The ESI-MS result of reaction product of OPD and formaldehyde.

Table S2 Recovery experiments of formaldehyde spiked in sleeve-fish and Chinese cabbage samples*.

Sleeve-fish sample

No.	Spiked/$\times10^{-5}$ M	Measured/$\times10^{-5}$ M	Recoveries/%
1	0	-0.26 ± 0.07	
2	1.2	1.10 ± 0.19	113.4
3	2.4	2.35 ± 0.09	108.6

Chinese cabbage sample

No.	Spiked/$\times10^{-5}$ M	Measured/$\times10^{-5}$ M	Recoveries/%
1	0	0.23 ± 0.14	
2	1.2	1.32 ± 0.18	90.6
3	2.4	2.48 ± 0.20	93.7

* The errors were obtained by measuring three parallel samples