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Electronic Supporting Information

Aggregation/dispersion-mediated peroxidase-like activity of MoS₂ quantum dots for colorimetric pyrophosphate detection

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Experimental Details

Chemicals and Materials

Ammonium tetrathiomoybdate ((NH₄)₂MoS₄, ≥99.0%), glucose, Sodium acetate (CH₃COONa, ≥99.0%), Acetic acid (CH₃COOH, ≥99.5%), Ferric sulfate hydrate (Fe₂(SO₄)₃ · xH₂O), hydrogen peroxide solution (H₂O₂, 30%) were all obtained from Kelong Chemical Co, Ltd. (Chengdu, China). Sodium pyrophosphate (Na₄P₂O₇ · 10H₂O, ≥99.0%) was obtained from Beibei Chemical Co, Ltd. (Chongqing, China) and 3,3',5,5'-tetramethylbenzidine dihydrochloride (TMB) were purchased from Aladdin (Shanghai, China). Deionized (DI) water (18.2 MΩ·cm) was used throughout the experiment.

Instrumentations

Transmission electron microscopy (TEM) images of the MoS₂ QDs were taken using a Tecnai G2 F20 transmission electron microscopy (USA) operated at 200kV. Atomic Force Microscopy (AFM) images of the MoS₂ QDs were measured by a Bruker Dimension Icon-AFM (USA). Dynamic light scattering (DLS) of MoS₂ QDs were taken using a Brookhaven Nano Brook omni (USA). The absorption spectra were measured using a UV-2550 UV-vis spectrophotometer (Shimadzu, Japan). X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, USA). Fluorescence of the QDs was measured with an LS-55 fluorescence spectrometer (PerkinElmer, USA). A high-speed TGL-16M centrifuge (Hunan, China) was used in the purification of samples.

Synthesis of MoS₂ Quantum dots

The MoS₂ Quantum dots were synthesized in one step by hydrothermal method with (NH₄)₂MoS₄ as the precursor. Typically, 0.05 g of (NH₄)₂MoS₄ was firstly dispersed in 10 ml of water. After ultrasound for 10 min, glucose was added into the solution as a reducing agent. Then, the mixture solution was transferred to a Teflon autoclave and allowed to react at 200 °C for 8 h. After being naturally cooled to room temperature, the mixture was centrifuged at 12000 rpm and the supernatant was collected for further characterizations and use.

Procedure for the detection of PPI

In a standard procedure, an appropriate concentration of PPI solution was added to a mixed solution (total volume, 3 mL) containing 100 μL MoS₂ QDs, 0.1 mmol/L TMB, 10 mmol/L H₂O₂ and 10 $\mu\text{mol/L}$ Fe³⁺ in acetate buffer (pH 4.0). After reacted for 20 min at room temperature, the final reaction solution was measured by a UV-vis spectrophotometer.

PPI assay in real water samples

The water samples were pretreated by filtered to remove insoluble impurities before PPI assay. The determination was carried out by adding 400 μL pretreated water sample into mixed solution (total volume, 3 mL) containing 100 μL MoS₂ QDs, 0.1 mmol/L TMB, 10 mmol/L H₂O₂ and 10 $\mu\text{mol/L}$ Fe³⁺ in acetate buffer (pH 4.0). Then, the mixed solution was incubated for 20 min at room temperature. Finally, the solution was measured by a UV-vis spectrophotometer.

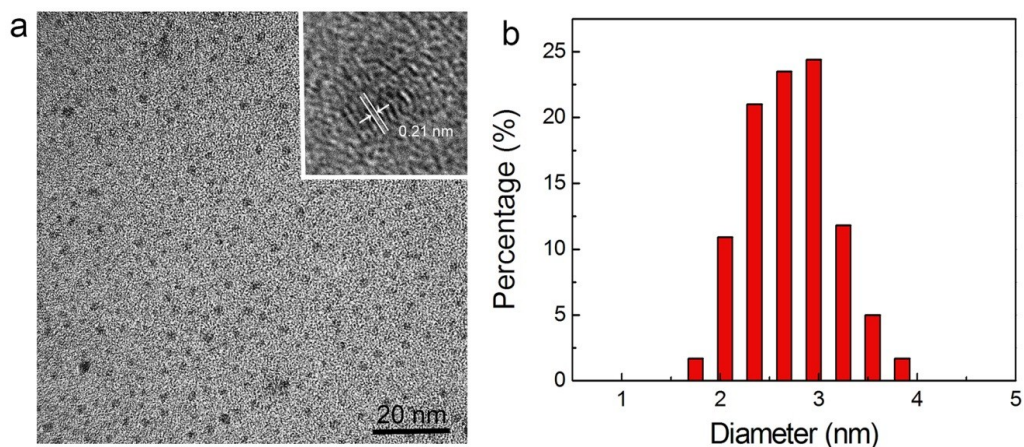


Fig. S1 (a) TEM image of the MoS₂ QDs. Inset of (a) is the HRTEM image of an individual QD. (b) A histogram that shows the size distribution of the QDs.

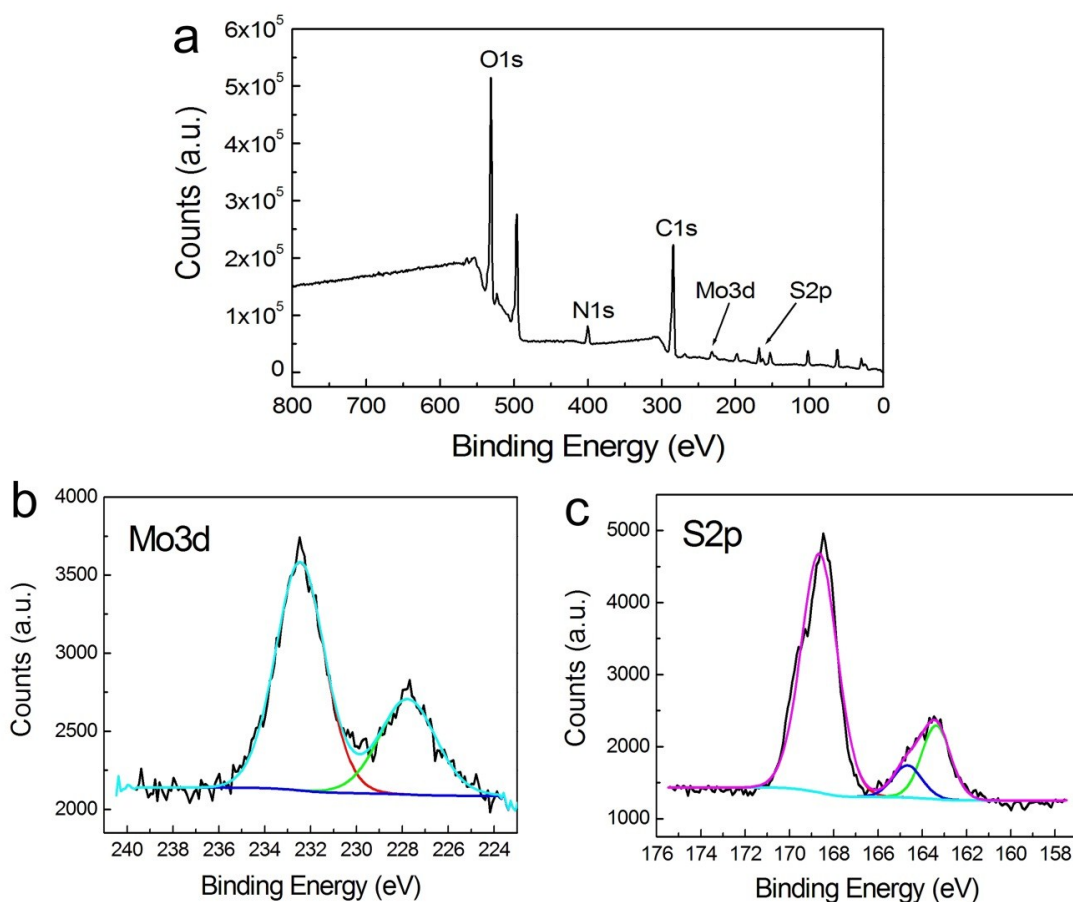


Fig. S2 XPS characterization of the MoS₂ QDs: (a) XPS spectrum showing all the elements in the MoS₂ QDs; (b, c) high-resolution XPS spectra of Mo3d and S2p.

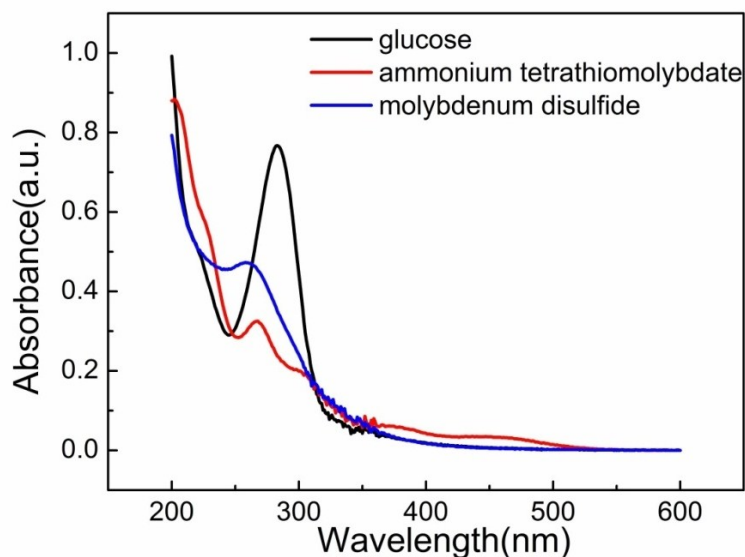


Fig. S3 UV-vis absorption spectra of glucose (black line), ammonium tetrathiomolybdate (red line) and the MoS₂ QDs (blue line).

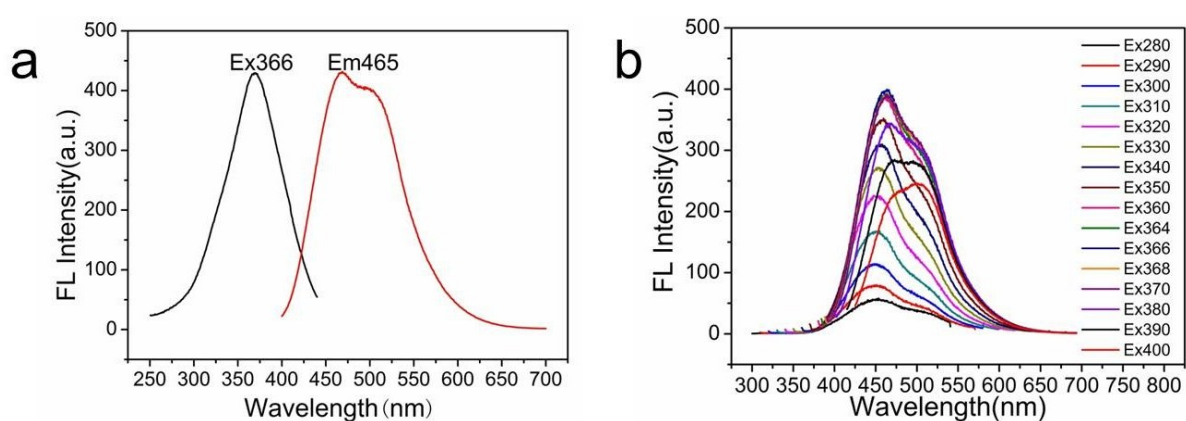


Fig. S4 (a) Fluorescence excitation and emission spectra of the as-prepared MoS₂ QDs. (b) Fluorescence emission spectra of the MoS₂ QDs with different excitation wavelengths.

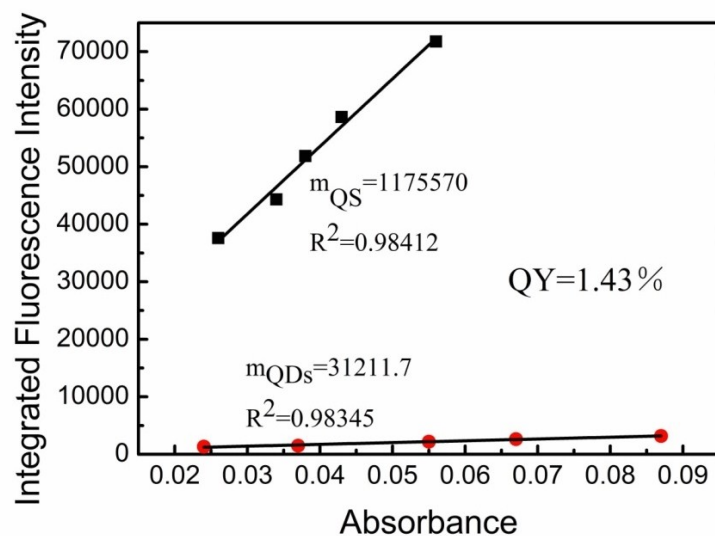


Fig. S5 Measurement of fluorescence quantum yield (QY) of the MoS₂ QDs using quinine sulfate (QS) as a reference.

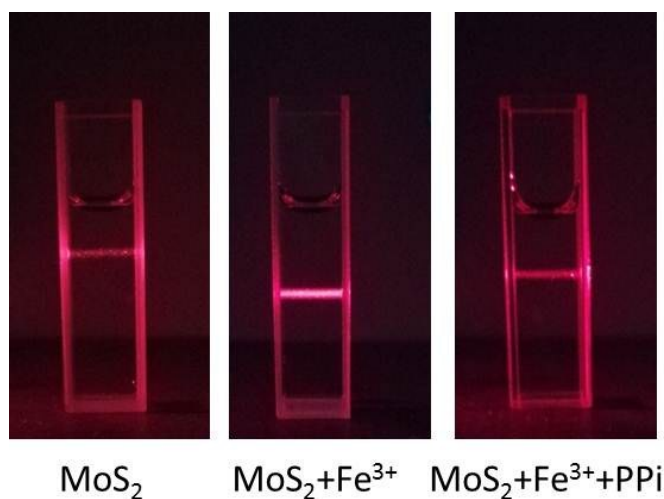


Fig. S6 Digital photographs of the Tyndall effect of MoS₂ QDs (left), the mix of MoS₂ QDs and Fe³⁺ (middle), and the mix of MoS₂ QDs, Fe³⁺ and PPI (right). The concentration of added Fe³⁺ and PPI were 1mM and 0.6 mM, respectively.

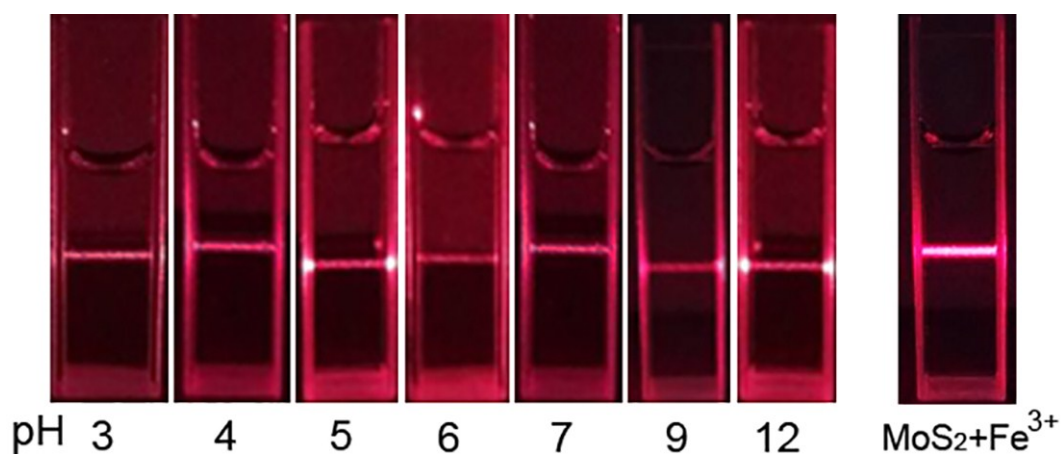


Fig. S7 Digital photographs of the Tyndall effect of MoS₂ QDs under different pH value. The rightmost sample contains both MoS₂ QDs and Fe³⁺, which is used as a contrast.

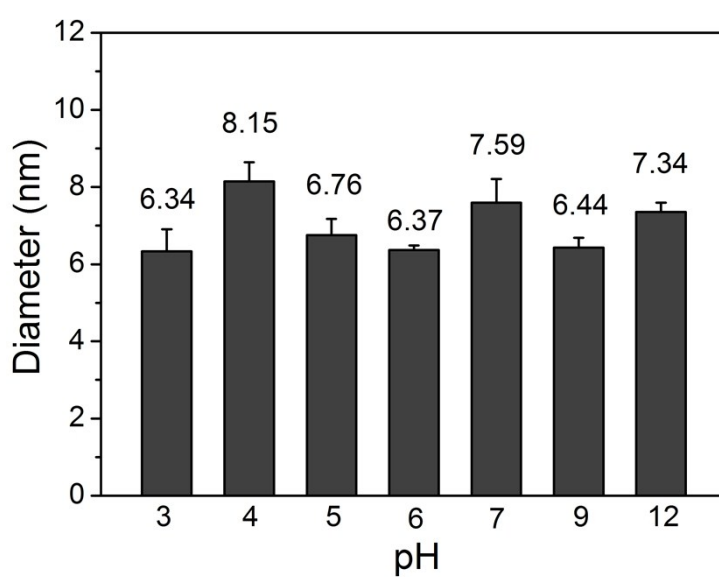


Fig. S8 The diameter of MoS₂ QDs under different pH that measured by DLS.

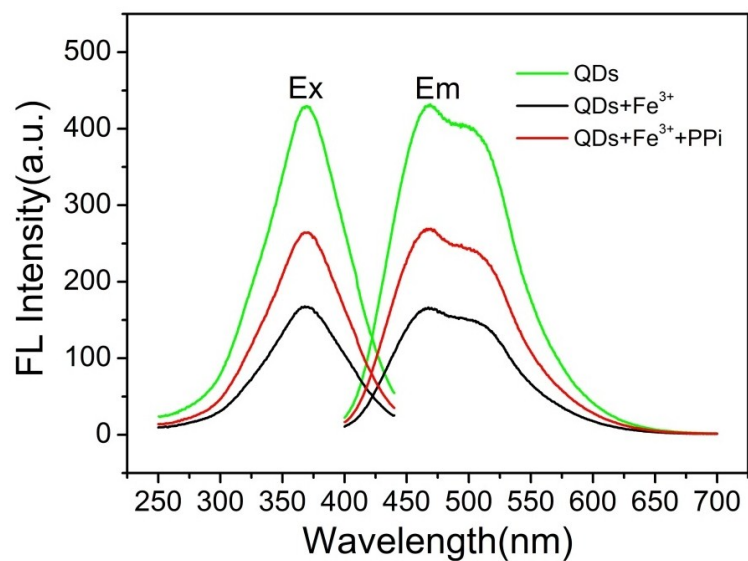


Fig. S9 Fluorescence spectra of MoS₂ QDs, MoS₂ QDs + Fe³⁺, and MoS₂ QDs + Fe³⁺ + PPI. The concentration of added Fe³⁺ and PPI were 1mM and 0.6 mM, respectively.

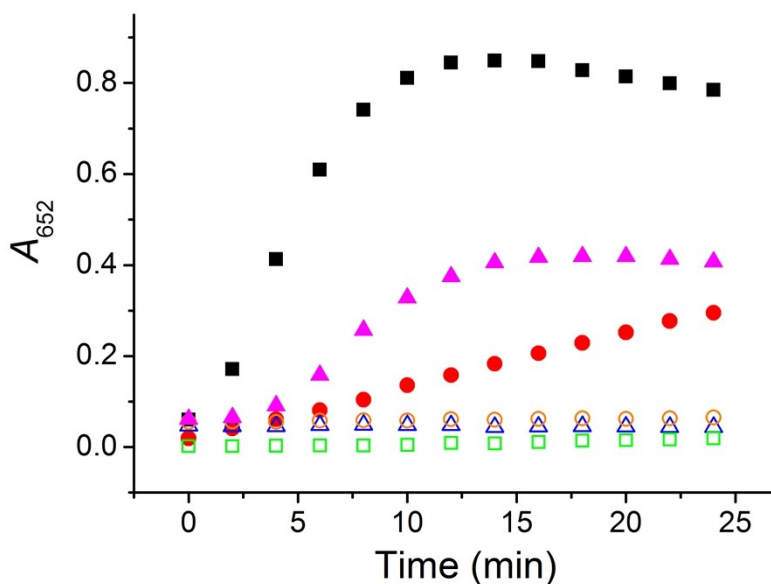


Fig. S10 The kinetic curves of TMB-H₂O₂ (□) and TMB-H₂O₂ in the presence of PPI (Δ), MoS₂ QDs (○), Fe³⁺ (●), MoS₂ QDs + Fe³⁺ (■), and MoS₂ QDs + Fe³⁺ + PPI (▲).

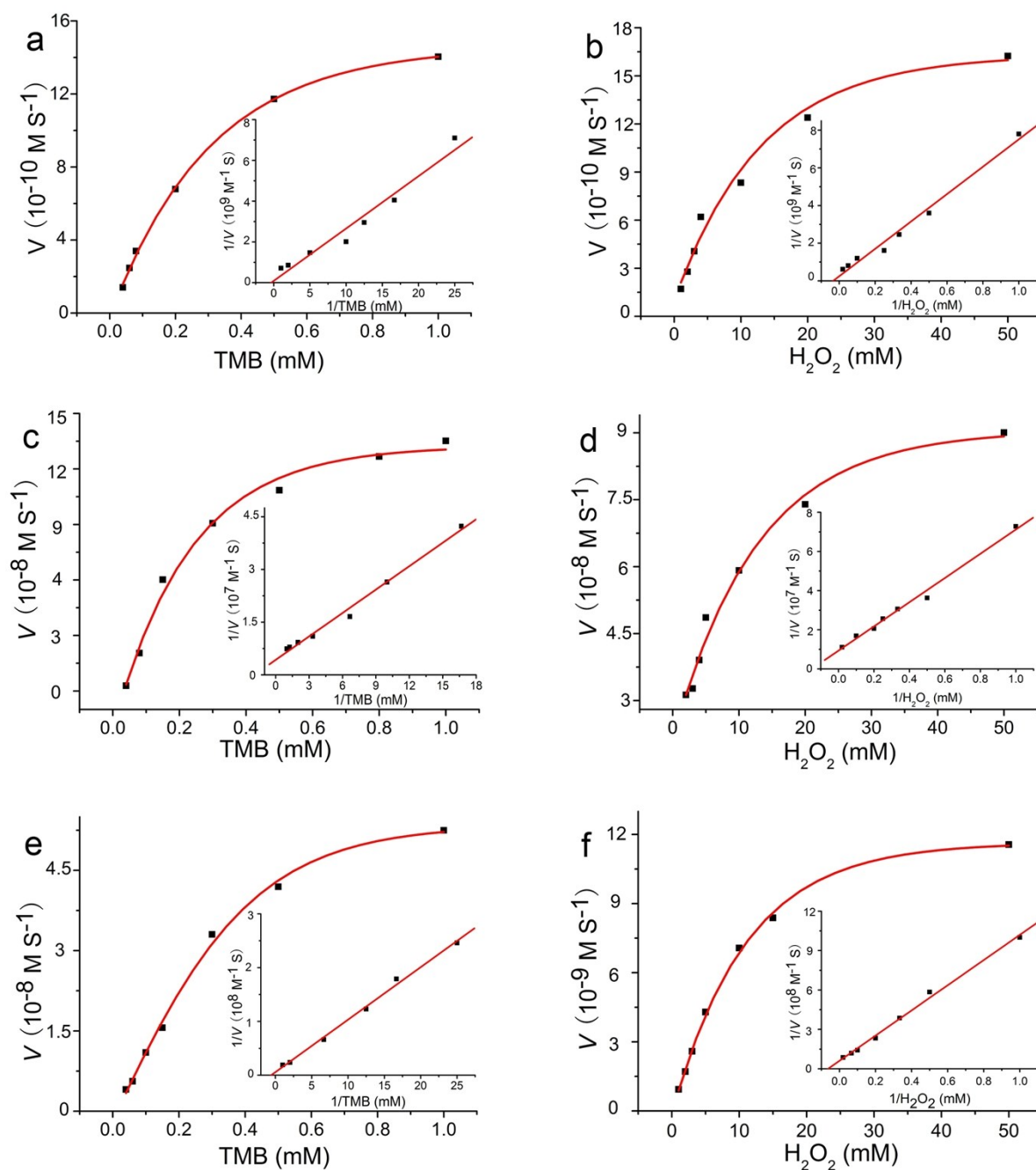


Fig. S11 Steady-state kinetic assays of the MoS₂ QDs (a, b), MoS₂ QDs and Fe³⁺ (c, d), MoS₂ QDs and Fe³⁺ coexist with PPI (e, f) for the oxidation of TMB by H₂O₂. The kinetic data were obtained by varying one substrate concentrations while keeping the other substrate concentration constant (0.1 mM TMB or 10 mM H₂O₂). Insets are the Lineweaver-Burk plots of the double reciprocal of the Michaelis-Menten equations.

Table S1 Comparison of the kinetic parameters of various catalytic systems toward the oxidation of TMB by H₂O₂.^a

	Substrate	K _m / mM	V _{max} / M s ⁻¹	K _{cat} / s ⁻¹	K _{cat} / K _m [s ⁻¹ mM ⁻¹]
MoS ₂	H ₂ O ₂	29.79	4.10×10 ⁻⁹	0.06	2.15×10 ⁻³
MoS ₂ + Fe ³⁺	H ₂ O ₂	6.64	1.07×10 ⁻⁷	1.68	2.52×10 ⁻¹
MoS ₂ + Fe ³⁺ + PPI	H ₂ O ₂	15.85	1.65×10 ⁻⁸	0.26	1.63×10 ⁻²
MoS ₂	TMB	3.00	1.17×10 ⁻⁸	0.18	0.06
MoS ₂ + Fe ³⁺	TMB	0.52	2.34×10 ⁻⁷	3.65	7.03
MoS ₂ + Fe ³⁺ + PPI	TMB	1.71	1.75×10 ⁻⁷	2.73	1.60

^a K_m is the Michaelis-Menten constant, V_{max} is the maximal reaction rate, K_{cat} is the catalytic constant, K_{cat} = V_{max}/ [E], and [E] is the concentration of MoS₂ QDs.

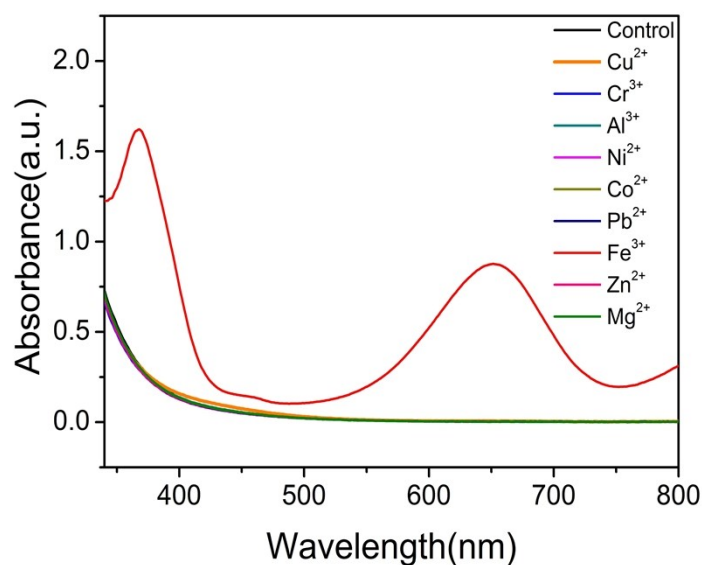


Fig. S12 UV–vis spectra showing the peroxidase-like activity of MoS₂ QDs in the presence of different metal ions.

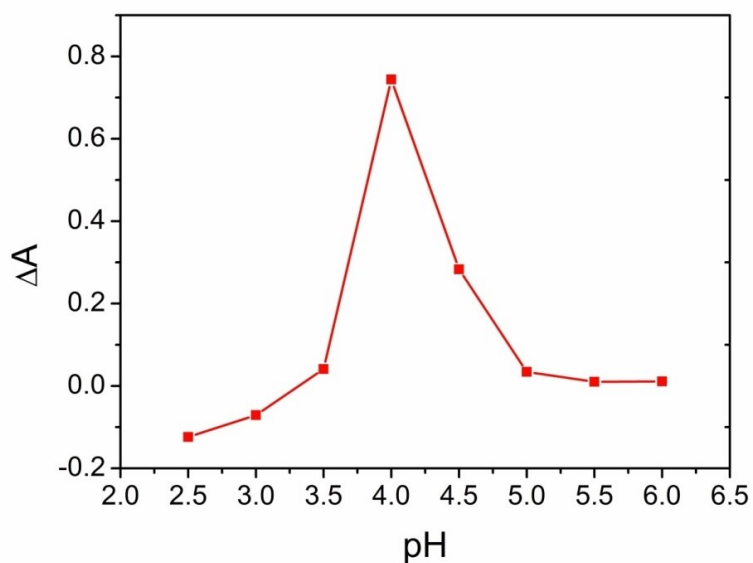


Fig. S13 The absorbance change of the system at 652 nm in the absence and presence of PPI under different pH values.

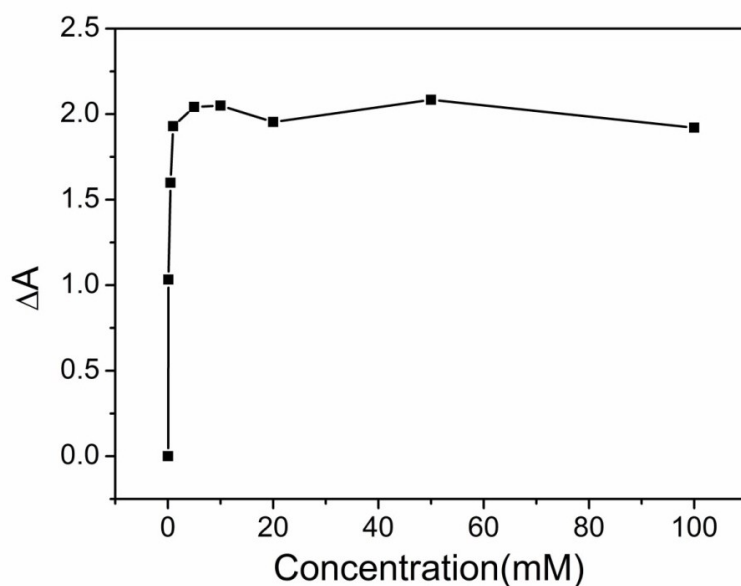


Fig. S14 The absorbance change of the system at 652 nm in the absence and presence of PPI with the addition of different concentration of H_2O_2 .

Table S2 Detection of PPI in spiked real water samples.

sample	PPI spiked (μM)	PPI measured (μM)	Recovery (%)	RSD (%,n=3)
	3.00	3.22	107.3	2.86
lake water ^a	5.00	4.74	94.70	1.67
	7.00	7.10	101.4	0.25
	3.00	3.22	107.3	5.12
tap water ^b	5.00	5.45	109.5	0.64
	7.00	6.86	97.99	0.13

^a The sample was collected from the campus lake.

^b The sample was collected from our lab.