Supporting information

DNA controllable peroxidase mimetic activity of MoS_2 nanosheets for constructing robust colorimetric biosensor

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Additional experimental details

Hydroxyl radical scavenging measurement. ESR spectrometer was utilized to detect hydroxyl radical under different conditions. DMPO was used to trap hydroxyl radical (•OH) to form DMPO/•OH spin adduct. The sample was prepared by separately adding various reagents (such as 100 μg/mL MoS_2, 10 mM Fe^{2+} or 10 μM DNA) into the mixture of H_2O_2 (200 mM) and DMPO (50 mM), and then ESR spectra measurements were conducted at room temperature.

Electrochemistry measurements. The three-electrode system was utilized for electrochemistry experiments, which was composed of platinum plate as auxiliary electrode, Ag/AgCl as reference electrode and glassy carbon as working electrodes. The MoS_2 NSs (10 μL, 1mg/ml) were dropped on the surface of polished glassy carbon electrode. After drying for 2 hours at room temperature, Nafion (2 μL, 5 wt%) was pipetted on it to prepare MoS_2 NSs modified electrodes. The cyclic voltammetric measurement of bare or MoS_2 NSs modified electrode was conducted in the 0.1 M phosphate buffer (pH 7.0) in the presence of 10 mM H_2O_2. All test solution was saturated with nitrogen by bubbling highly pure nitrogen for 30 min to eliminate oxygen interference.

CEA Detection in serum samples. CEA detection in serum samples was carried out through standard addition method. In brief, CEA (500 ng/mL), 2 μL 100-fold dilution of serum samples, and the mixture of CEA (500 ng/mL) and2 μL 100-fold dilution of serum samples was separately incubated with 25 μg/mL aptamer modified MoS_2 NSs in 10mM Tris-HCl buffer at 37 ºC for 30 minutes. Then the above reaction mixture was added in 0.1M acetate buffer (pH 4.0) containing 0.2 mM H_2O_2 and 0.4 mM TMB. After 15 minutes incubation at 37 ºC, the UV-vis absorption spectrum was determined immediately.

Preparation of portable test kits and visual detection of CEA. The portable test kit for CEA detection was prepared as follows: agarose (20 mg) was dissolved in boiling water (2mL). When the solution was cooled to 40 ºC, the hybrid of 7.5 μL MoS_2

NSs (1 mg/mL) and 30 μL CEA aptamer (25 μM), 30 μL TMB (20 mM) were added and mixed. The mixture solution (200 μL) was transferred into the cap of the microcentrifuge tube. The hydrogel was shaped after drying under ambient temperature for 5 minutes. For CEA detection, 50 μL CEA with different concentrations was added in the hydrogel. After 60 minutes incubation at 37 ºC, 30 μL H_2O_2 (10 mM) and 300 μL 0.1M acetate buffer (pH 4.0) were added into the test kit. After closing the cap, the test kit was turned upside down and incubated at 37 ºC for 60 minutes.

DNA adsorption. DNA adsorption by MoS_2 nanosheets was investigated by monitoring the change of fluorescence signal of cy5-DNA solution after the addition of MoS_2 nanosheets. The fluorescence intensity at 662 nm of 75 nM Cy5-DNA solution before adding MoS_2 nanosheets was monitored for 10 min as initial intensity. The effect of salt concentration on the kinetics of DNA adsorption was investigated by detecting the change of fluorescence intensity of 75 nM Cy5-DNA in10 mM Tris solution with various salt concentrations after adding MoS_2 NSs (15 ug/mL).

DNA desorption. The 75 nM Cy5-DNA in 10mM Tris-HCl buffer (containing100 mM NaCl, 5 mM KCl and 5 mM $MgCl_2$) was incubated with MoS_2 NSs (15 ug/mL) for 10 min at room temperature. The fluorescence intensity at 662 nm of the mixture was monitored for 10 min as initial intensity. The precipitation was collected by centrifugation the above mixture and then dispersed in 100 μL Tris-HCl buffer. Various reagents, including10 mM NaOH , 10 mM phosphate, 1 mM guanosine, 5 M urea, 50% DMSO, 0.01% CTAB, 0.01% SDS, 0.01% Tween 20 and 0.01% Triton X-100, were separetely added in the dispersion to induce DNA desorption. Subsequently, the fluorescence intensity was determined immediately.

Supporting figures

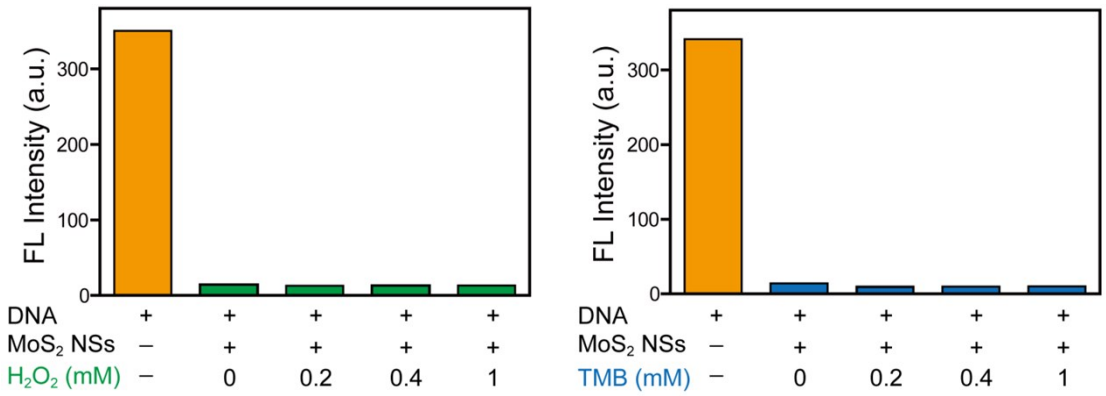

Fig. S1 The effect of different H_2O_2 and TMB on Cy5 labeled DNA adsorption by MoS_2 NSs.

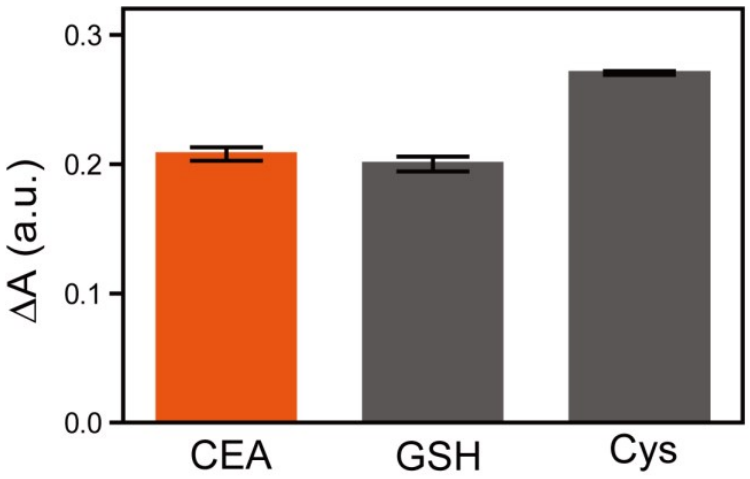

Fig. S2 Specificity of the proposed biosensor for glutathione and cysteine.

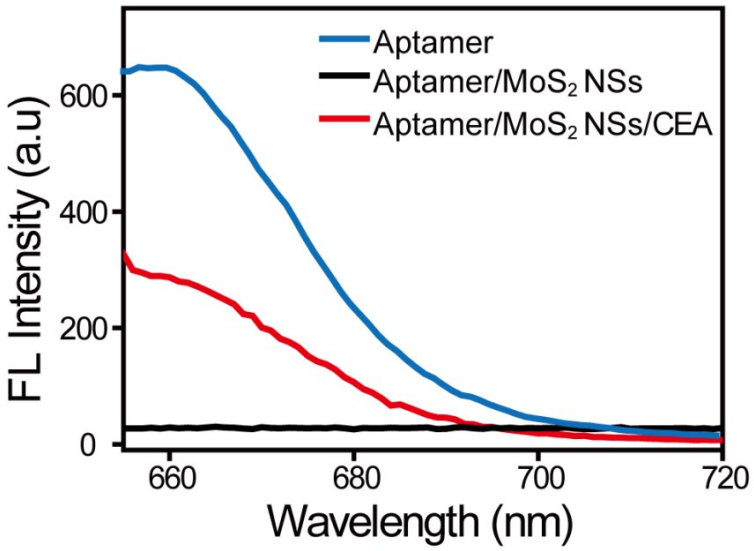

Fig. S3 Fluorescent spectra of cy5 labeled CEA aptamer under different system.

Table S1 Comparison of steady kinetic parameters of MoS_2 NSs and DNA/MoS_2 NSs nanozymes.

Catalyst	Substrate	K_m (mM)	V_{max} (10^{-8} M/s)
MoS_2 NSs	H_2O_2	0.0058	1.2095
DNA/MoS_2 NSs	H_2O_2	0.0348	5.8955
MoS_2 NSs	TMB	2.9755	9.3301
DNA/MoS_2 NSs	TMB	0.6518	10.5474