Electronic Supplementary Materials

Layered MnO_2 nanosheet as a label-free nanoplatform for rapid detection of mercury(II)

Ke Yang,[*ab] Ming Zeng,[a] Xiaojian Hu,[a] Baoshou Guo[a] and Jianbo Zhou[a]

[a]*College of Basic Medical Sciences, Changsha Medical University, Changsha 410219, China*

[b]*College of Biology, Hunan University, Changsha 410082, China.*

E-mail: yangkenhm@163.com; Fax: +86 731-88498988; Tel: +86 731-88498988

Experimental Section

Materials. 2-(N-morpholino)ethanesulfonic acid (MES), potassium permanganate ($KMnO_4$) and SYBR Green I were purchased from Alfa Aesar. $AgNO_3$, $LiNO_3$, $Ca(NO_3)_2$, $Mg(CH_3COO)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Cd(NO_3)_2$, $Co(NO_3)_2$, $Mn(CH_3COO)_2$, $Ni(NO_3)_2$, $Pb(NO_3)_2$, $Hg(NO_3)_2$ and $CrCl_3$ were of analytical grade and used as received. All solutions were prepared with MilliQ water (resistance > 18 MΩ cm^{-1}) from a Millipore system. Other chemicals were used as received without further purification. DNA was synthesized by Sangon Biotechnology Co., Ltd. (Shanghai, China). The dye-labeled mercury-specific oligonucleotide (MSO) sequence: 5'-FAM-TACTTC TTTCTT CCCCCC TTGTTT GTTGTA-3'. The dye-labeled mercury-nonspecific oligonucleotide (non-MSO) sequence: 5'-FAM-TCTCTT CTCTTC ATTTTT CAACAC AACACA-3'.

Apparatus. Transmission electron microscopy (TEM) images were obtained from a JEOL 3010 microscope with an accelerating voltage of 100 kV. Scanning electron microscopy (SEM) was performed with a JSM-6700F microscope. Powder X-ray diffraction (XRD) patterns of as-prepared samples were recorded on a Scintag XDS-2000 powder diffractometer using Cu Kα irradiation (λ = 0.154 nm). The 2θ range and recording step were 5−80° and 0.004°, respectively. Crystallite size was calaulated using the Scherrer equation. N_2 adsorption−desorption isotherms were obtained at −196 °C on a Micromeritics ASAP 2010 sorptometer by static adsorption procedures. Samples were degassed at 100 °C and 10^{-3} Torr for a minimum of 12 h prior to analysis. Brunauer−Emmett−Teller (BET) surface areas were calculated from

the linear part of the BET plot according to IUPAC recommendations.The fluorescence spectra were recorded with a Hitachi F-4500 spectrophotometer equipped with a Xenon lamp excitation source. The excitation wavelength was 494 nm, and the fluorescence measurements were carried out at 24 °C.

Preparation of MnO_2 nanosheets. In a typical experiment, 250 μL of $KMnO_4$ solution (10 mM) was added to a 1.5 mL microcentrifuge tube containing 250 μL of MES buffer (0.1 M, pH 6.0). The resulting mixture was sonicated for 30 min until a brown colloid was formed. Subsequently, the obtained suspension (layered MnO_2) was centrifuged, washed for three times with deionized water to remove the unreacted reagent, and redispersed in water just before further characterizations and applications. Moreover, to improve the water dispersibility, the purified MnO_2 nanosheets were sonicated for 30 min. The supernatant was collected as MnO_2 nanosheets stock suspension.

Fluorescence assay for Hg^{2+}. For the sensitivity measurement, different concentrations (0, 1, 5, 10, 20, 50, 100, 250, 500 and 1000 nM) of Hg^{2+} were incubated in 1 mL of Tris-HNO_3 buffer (pH 8.0) containing 20 mM of $NaNO_3$ and 10 nM of MSO for 5 min at 24 °C. Then 20 μL of MnO_2 nanosheets (0.1 mg mL^{-1}) was added to this mixture and the fluorescence measurement was carried out 5 min after the addition of MnO_2 nanosheets at 24 °C. For real environmental samples assays, river water samples were collected from Xiangjiang River in Changsha, China. ICP–MS analysis showed no detectable mercury. Then, $Hg(NO_3)_2$ was added to simulate contaminated water. For Hg^{2+} detection, the water samples were used to prepare the

Tris-HNO_3 buffer (pH 8.0) and then spiked with varying Hg^{2+} concentrations. The selectivity was checked by addition of 10 μM Li^{+}, Ag^{+}, Ca^{2+}, Cd^{2+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+} and Fe^{3+}.

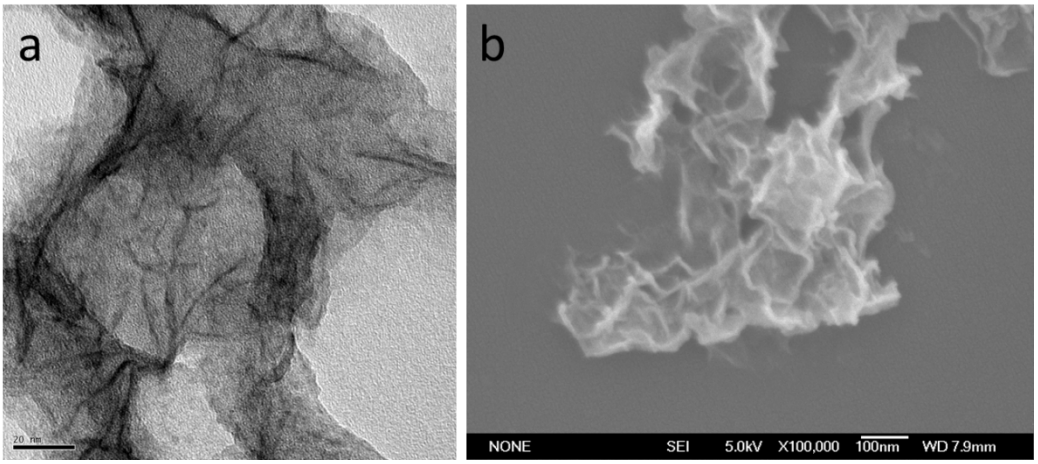

Fig. S1. TEM and SEM images of the as-prepared MnO_2 nanosheet.

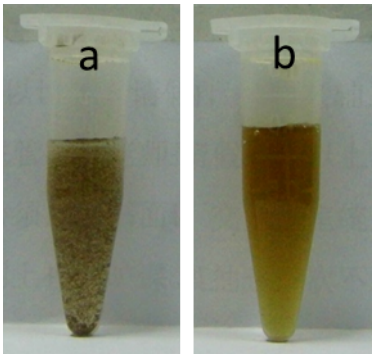

Fig. S2. Digital photograph showing the dispersion of MnO_2 nanosheets without (a) and with (b) sonication for 30 min after being laid up for 20 min.

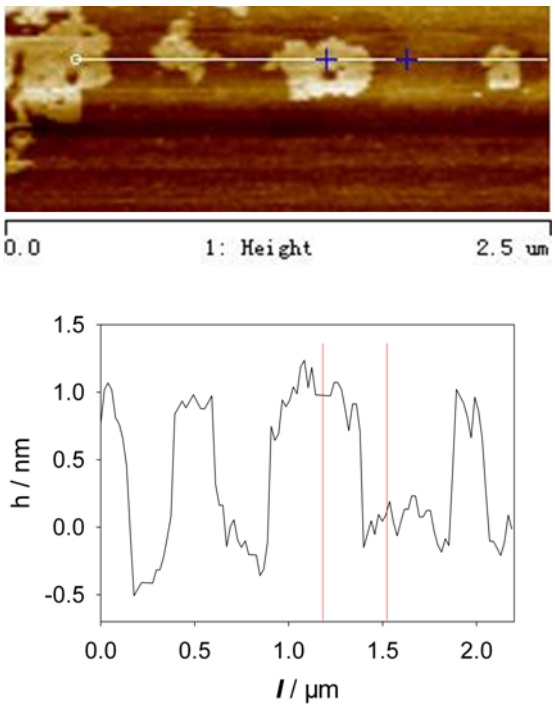

Fig. S3. AFM height image of MnO_2 nanosheets deposited on mica substrates.

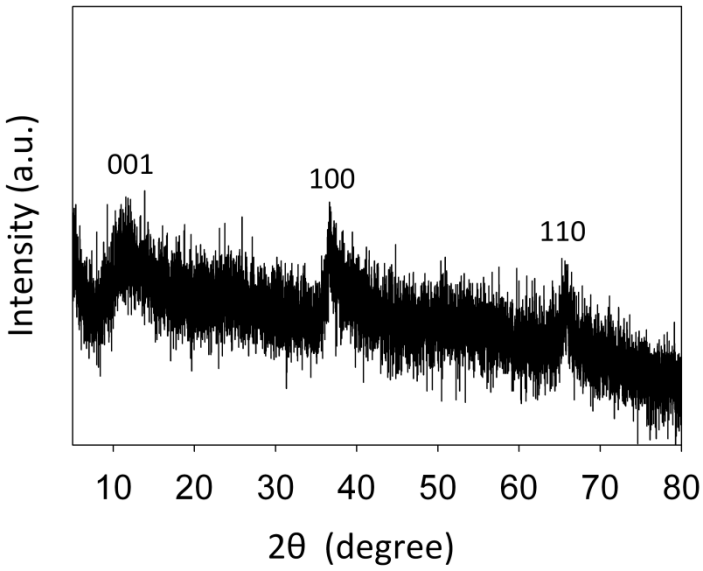

Fig. S4. XRD patterns of as-prepared MnO_2 nanosheets.

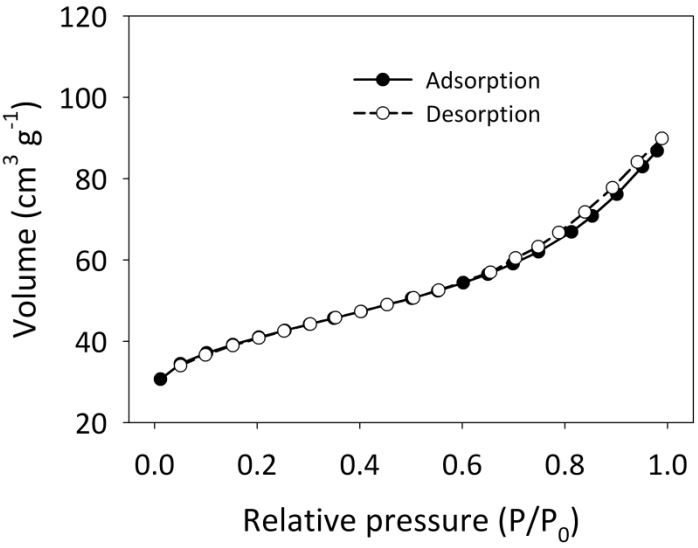

Fig. S5. Nitrogen sorption isotherm of the obtained MnO_2 nanosheets.

Effect of Hg^{2+} Ions on the Fluorescence of FAM-labeled MSO probe. Whether the fluorescence of FAM-labeled MSO probe was greatly quenched by Hg^{2+}. Fig. S6 shows the fluorescence emission spectrum of FAM-labeled MSO probe in the presence of Hg^{2+} (500 nM). No obvious emission change could be observed. The results demonstrate that the proposed strategy could be used to detect Hg^{2+} in aqueous solution.

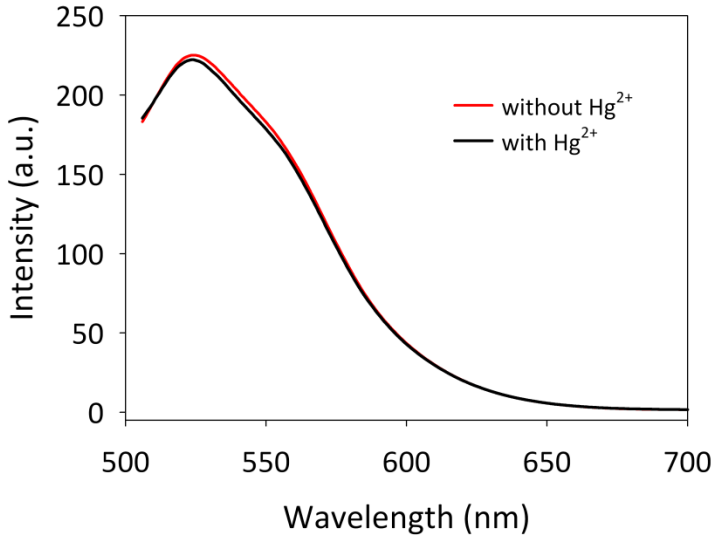

Fig. S6. Fluorescence emission spectra of FAM-labeled MSO probe (10 nM) in the absence and presence of Hg^{2+} (500 nM).

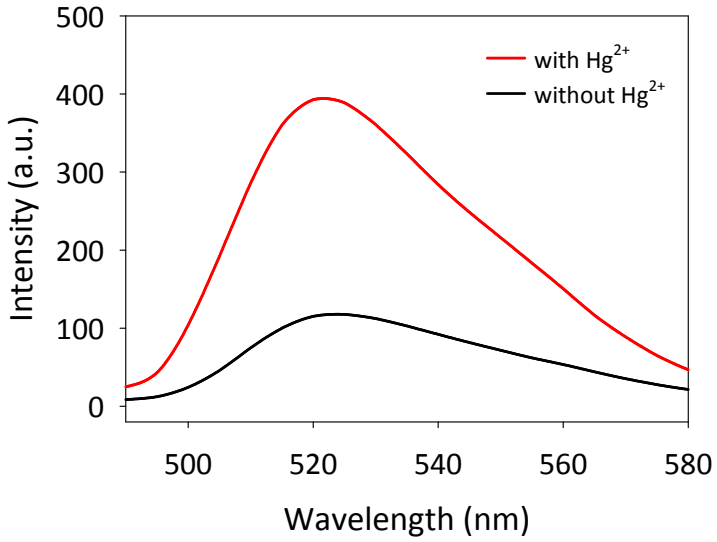

Fig. S7. Fluorescence spectra of nonlabeled MSO probe (10 nM) in the absence and presence of Hg^{2+} (500 nM) after being stained with SYBR Green I for 10 min.

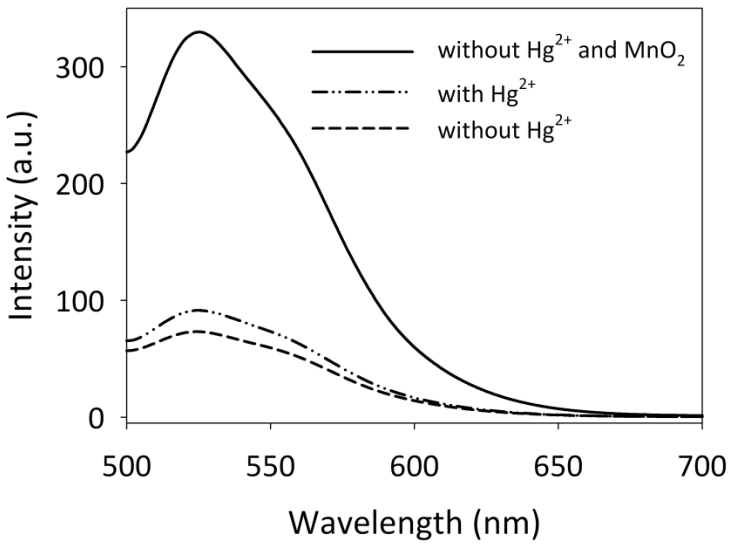

Fig. S8. Fluorescence spectra of FAM-labeled non-MSO probe (10 nM) in the absence and presence of Hg^{2+} (500 nM) after being incubated with MnO_2 nanosheet (0.1 mg mL^{-1}) for 10 min.

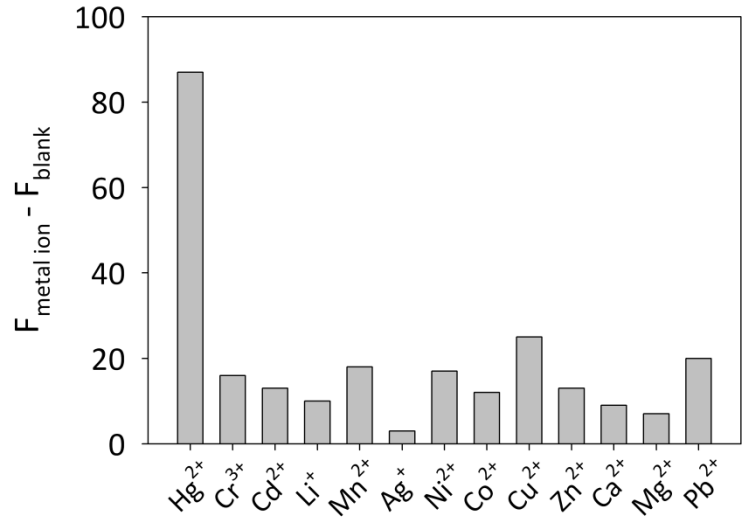

Fig. S9. Selectivity of the analysis of Hg^{2+}. The concentrations of metal ions were all 50 nM.

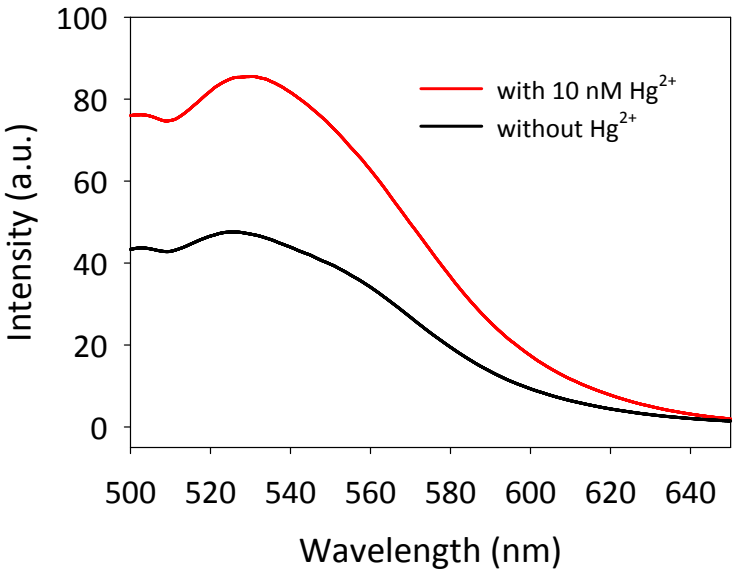

Fig. S10. Fluorescence spectra of MSO probe upon incubation with and without Hg^{2+} (10 nM) in environmental water sample and then mixed with MnO_2 nanosheet (0.1 mg mL^{-1}).

Table S1. Comparison of different Hg^{2+} detection methods using various nanomaterials

Nanomaterials	Linear range (nM)	Detection limit (nM)	Assay time (min)	Sensing mode	Ref.
Gold nanoparticles	96-6400	40	30	Turn on	19a
Gold nanoparticles	2-60	2	10	Turn off	19b
Silica nanoparticles	0-500	20	20	Turn on	12c
Silver nanoclusters	10-300	10	500	Turn on	10d
Carbon dots	0-25	0.23	—	Turn off	19c
Carbon nanotubes	50-8000	14.5	20	Turn on	19d
Graphene oxide	1-50	0.92	5	Turn off	19e
Graphene oxide	10-2000	0.5	10	Turn off	15
Graphene oxide	0-1	0.3	140	Turn on	19f
Quantum dots	50-800	1.5	30	Turn off	8d
MnO_2	0-20	0.8	6	Turn on	This work

Table S2. Recovery experiments of Hg^{2+} in river water samples[a]

Samples	Hg^{2+} spiked (nM)	Hg^{2+} detected (nM)	Recovery (%)
1	10	9.8 ± 1.2	98 ± 0.12
2	15	14.3 ± 1.8	95 ± 0.19
3	20	19.4 ± 2.6	97 ± 0.15

[a]Mean values and standard deviations were obtained from three independent experiments.