Electronic Supplementary Material (ESI) for ChemComm.

Nanometer-sized manganese oxide-quenched fluorescent oligonucleotides: an effective sensing platform for probing biomolecular interactions

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Experimental part:

Materials

The oligonucleotides were obtained from Sangon Biotechnology Inc. (Shanghai, China). Adenosine, uridine, guanosine, and cytidine were purchased from Sigma-Aldrich. 2-(N-morpholino)ethanesulfonic acid (MES), potassium permanganate ($KMnO_4$), and *N*-cetyltrimethylammonium bromide (CTAB) were purchased from Alfa Aesar. All buffers were prepared with ultra-pure MilliQ water (resistance >18.2 MΩ cm^{-1}). Other chemicals were used as received without further purification.

Preparation of nano-MnO_2 materials

In a typical procedure, 0.5 g of $KMnO_4$ was dissolved in 450 mL of distilled water, and the mixture was stirred for about 0.5 h. A total of 1.5 g of CTAB was added, and a steady emulsion was formed. 50 mL of MES buffer (0.1 M, pH 6.0) was then added to the mixture solution. The resulting mixture was reacted for 12 h until a brown-black colloid was formed. Subsequently, the crude product was collected by centrifugation, washed several times with deionized water and alcohol to remove any possible residual reactants, and redispersed in 500 mL of deionized water.

Fluorescent DNA assays

The fluorescent probe P1 (20 nM) was hybridized with different T1 concentrations for 10 min prior to the addition of the nano-MnO_2 solution (0.1 mg mL^{-1}). The final concentration of T1 ranged from 0.5 nM to 50 nM. For kinetic study of fluorescence quenching, fluorescence spectra were obtained immediately after the addition of nano-MnO_2. For DNA detection, the fluorescence intensities of mixed solutions were recorded after being incubated with nano-MnO_2 for 5 min. All measurements were performed in 20 mM Tris-HCl buffer (pH 7.4, 100 mM NaCl, 10 mM $MgCl_2$) at room temperature. The

fluorescence spectra were measured using a Hitachi F-7000 spectrophotometer. Excitation and emission wavelengths are 494 and 526 nm, respectively.

Adenosine assays

FAM-labeled AA (100 nM) was incubated with different concentrations of adenosine for 20 min. After the resulting solutions were incubated with nano-MnO_2 materials (0.1 mg mL^{-1}) for 5 min, fluorescence intensities of the mixtures were also measured at room temperature. The final concentration of adenosine ranged from 5 μM to 1 mM. Excitation and emission wavelengths are 494 and 523 nm, respectively.

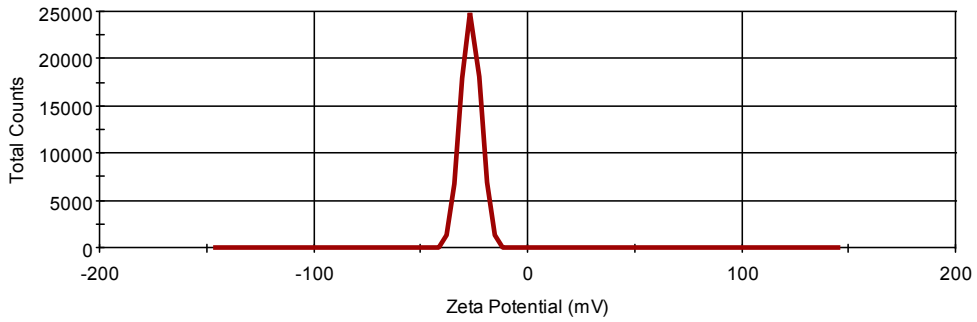

Fig. S1. Zeta-potential of nano-MnO_2 materials. The zeta potential of nano-MnO_2 was −23.6 eV.

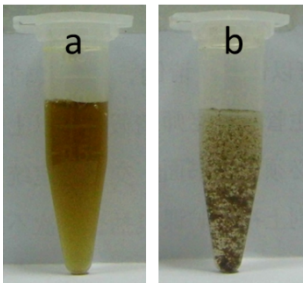

Fig. S2. Digital photograph showing the dispersion of nano-MnO_2 (a) and MnO_2 nanosheet (b) in water.

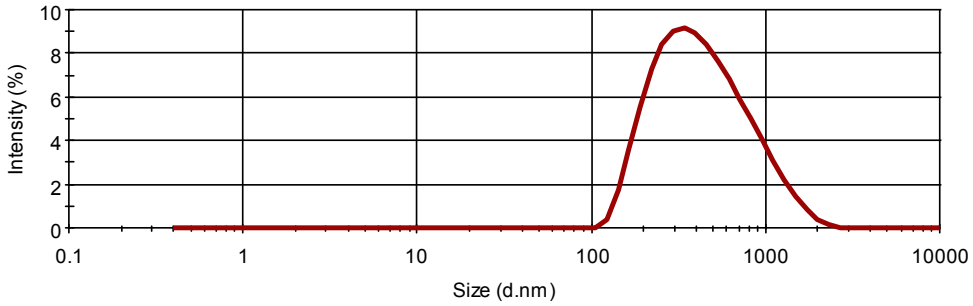

Fig. S3. DLS of nano-MnO_2 materials in water.

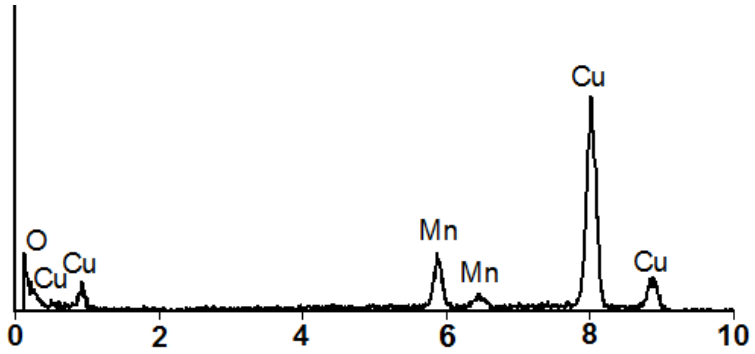

Fig. S4. SEM-assisted EDS analysis of as-prepared nano-MnO_2 materials. The peaks of Cu element result from the copper sheet substrate.

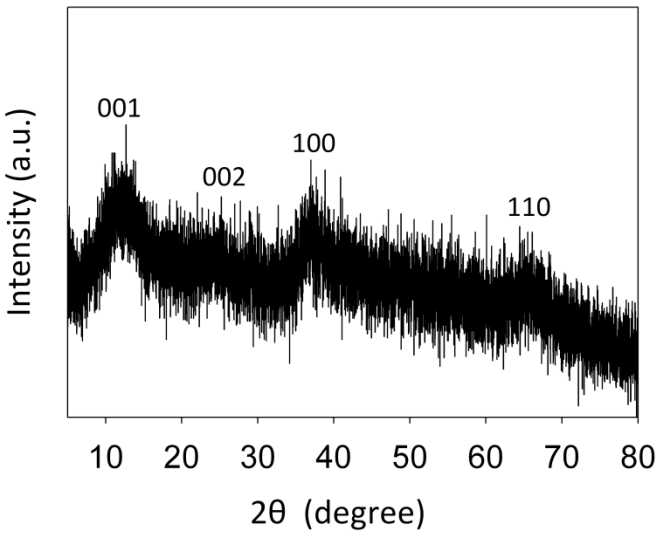

Fig. S5. Wide-angle XRD patterns of nano-MnO_2 materials.

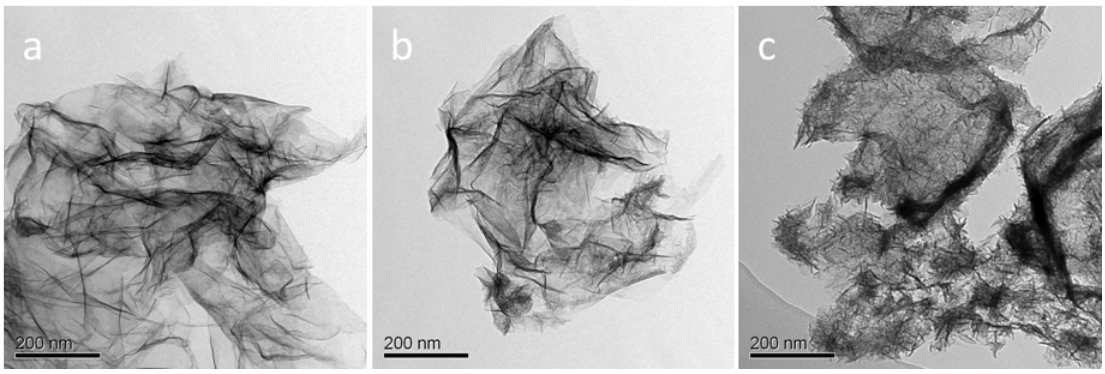

Fig. S6. TEM images of MnO_2 nanostructures at different concentrations of CTAB of 0 (a), 1.0 (b), and 2.0 mg mL^{-1} (c), respectively.

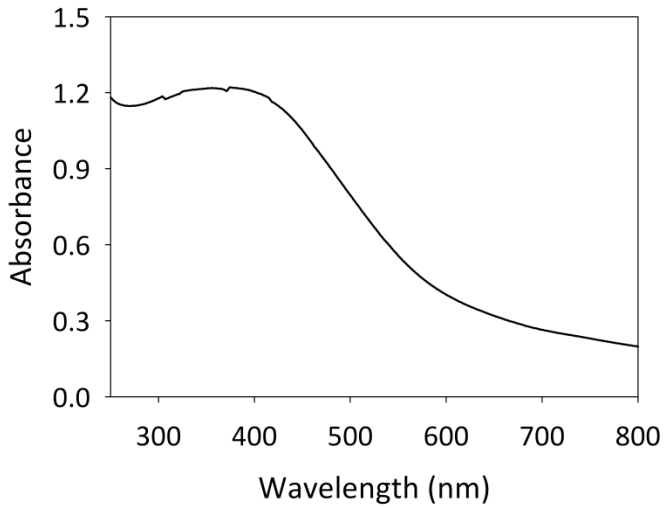

Fig. S7. UV-vis absorption spectrum of nano-MnO_2 materials in water.