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Supplementary Information

Portable and Quantitative Monitoring of Mercury Ions Using DNA-capped Mesoporous Silica Nanoparticles with a Glucometer Readout

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1. Experimental process

1.1. Chemicals and reagents

Tetraethoxysilane (TEOS) and n-cetyltrimethylammoniumbromide (CTAB) were purchased from Sinopharm (Shanghai, China). 3-Aminopropyltriethoxysilane (APTES) was obtained from Sigma-Aldrich (Shanghai, China). The Exonuclease III and 10×NEB buffer 1 (100 mM bis-tris-propane-HCl, 100 mM $MgCl_2$, 10 mM dithiothreitol, pH 7.0) were purchased from New England Biolabs. Ultrapure water were obtained from a Millipore water purification system (≥18 MΩ,Milli-Q, Millipore). Hybridization buffer (HB, pH 7.4) was based on 10 mM Tris-HCl that supplied with 50 mM NaCl and 10 mM $MgCl_2$. Other chemicals were purchased from standard commercial sources and were analytical grade purity. The commercial personal glucose meter used in this study was an ACCU-CHEK Active glucose meter (Roche, Germany). And oligonucleotides were obtained from Sangon Biotechnology (Shanghai, China). Oligonucleotide sequences used in this study were as follows:

Table S1. Sequences of the DNA used in this study.

Name	Sequence (5'→3')
wrapping DNA	GACACACTAGACTACTTTTCG
assistant DNA	CGAAAAGTAGTCTAGAACACA
1-mismatch DNA	CGTAAAGTAGTCTAGAACACA
2-mismatch DNA	CGTTAAGTAGTCTAGAACACA
3-mismatch DNA	CGTTTAGTAGTCTAGAACACA

Note: underline indicates the mismatch nucleotide.

1.2. Preparation of of aminated mesoporous silica nanoparticles (MSNs)

MSNs were synthesized according to the previous literature.[1] Firstly, 1.75 mL of NaOH (2.00 M) was added to 240 mL of CTABr (2 mg/mL $^{-1}$) and heated to 95 °C. Under continuous stirring, 2.5 mL of TEOS was added drop wisely. The mixture was allowed stirring for 3 h to give a white precipitate. Then, the solid product was collected by centrifugation. It was washed with deionized water and ethanol step wisely, and dried at 60 °C overnight. The obtained white powder was finally calcined at 550°C using oxidant atmosphere for 5 h to remove the template phase. After then, 0.5 g of calcined MSNs and 0.5 mL of APTES were suspended in 50 mL of anhydrous ethanol inside a round-bottom flask. The mixture was stirred continuously for 6 h at 36°C, followed by collection with filtration. The resulted nanoparticles (aminated MSN) were washed with ethanol and dried at 60°C.

1.3. Preparation of glucose-loading MSNs capped with wrapping DNA

The loading of glucose molecules into pores of aminated MSN was prepared according to Tang et al.[2] Briefly, 5 mg of aminated MSNs was initially dispersed into 500 mL of extension buffer (pH 7.5) containing 2.0 M glucose. The mixture was then shaken gently on an end-over-end shaker overnight at room temperature, which allowing glucose molecules diffuse into the pores of the aminated MSNs. After then, 20 μL of wrapping DNA (200 μM) was added into the suspension. The mixture was stirred gently for 8 h at 4°C. The DNA-wrapped MSNs was centrifuged and washed with distilled water to remove excess DNA strands and glucose until a low background PGM signal was obtained. Finally, the DNA-capped MSNs loaded with glucose (designated as DNA-MSNs) was re-

dispersed in 200 μL extension buffer (pH 7.5) ($C_{[MSN]}$ ≈25 mg/mL^{-1}) for further use.

1.4. Procedure for Hg^{2+} detection

The analytical procedure is depicted schematically in Scheme 1. Initially, 10 μL of the as-prepared MSN suspension was added into a 200 μL PCR tube, then 5 μL of Hg^{2+} standards (or samples) and assistant DNA (200 nM) were added into the tube. It was incubated at room temperature for 30 min. Subsequently, 20 units of Exo III were added to the above solution, and the mixture was incubated for another 30 min at room temperature on an end-over-end shaker. After reaction, the resultant mixture was centrifuged at 5000 rpm for 5 min. Five microliters of the supernatant was used for glucose measurement using a commercialized Roche PGM. All measurements were conducted at room temperature in triplicate.

1.5. Analysis of environmental water samples

Tap water was obtained from our laboratory. Lake water was collected from Guangzhou voluntary tree planting Park (Guangzhou, China). Those environmental water samples were filtered through a 0.2 μm membrane to remove the insoluble impurities. Aliquots of the water samples were spiked with different concentrations of Hg^{2+}. Ninety microliters of spiked water was initially mixed with 10 μL hybridization buffer, and then detected by using protocol described.

1.6. MSNs characterization

Transmission electron microscopy (TEM) was performed using a LEO 912-Omega (Carl Zeiss, Jena, Germany) microscope. A drop of nanoparticles suspension was placed on a carbon-coated copper grid and dried under vacuum. Micrographs were obtained at 120 KV.

Zeta potential was measured using a Mastersizer 2000 laser diffractometer (Malvern Instruments, Worcestershire, UK). Nanoparticles were prepared and analyzed in distilled water at 25°C. The volume of sample was 1 mL containing a final MSNs concentration of 10 μg/mL.

For X-ray diffraction (XRD) of MSNs, nanoparticle solution was spread evenly on a glass slide and dried by under vacuum. XRD patterns were recorded using an Empyrean, PANalytical XRD System with Cu-Kα radiation. It was operated at a voltage of 40 kV and a current of 40 mA and the diffracted intensities were recorded from 0.5° to 10° 2θ angles.

2. Partial Results

2.1. Capacity of MSNs for glucose loading and releasing

MSNs without DNA wrapping had the highest PMG signal, which was reduced significantly after DNA blocking. The PGM signal in the presence of complementary oligonucleotide (c-DNA, 20 μM) and single mismatch assistant DNA (200 nM DNA, 10 nM Hg^{2+}) were 6.5±0.2 mM and 14.1±0.6 mM, respectively. The Hg^{2+} trigged glucose leakage from DNA-MSNs was comparable to that of c-DNA, which indicated the successful capping and high efficient releasing capability of this method.

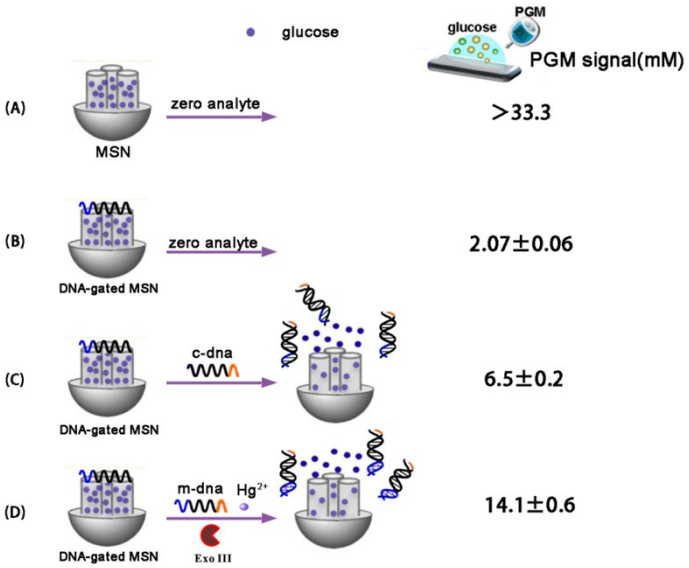

Fig. S1 Study of the loading capacity of MSNs toward glucose molecules. (A) MSN loading with glucose toward the zero analyte. (B) DNA-MSN loading with glucose toward the zero analyte. (C) DNA–MSNs loading with glucose and 20 μM assistant DNA. (D) DNA–MSNs loading with glucose in the presence of Hg^{2+} (10 nM) and 2-mismatch DNA (200 nM). Incubation time was 6 h.

2.2. Recovery of the assay

Tap water and lake water were spiked with 5 nM, 20 nM and 80 nM Hg^{2+}, respectively. Satisfactory recovery rates between 96% and 108% were obtained, which shows its feasibility for real environmental samples.

Table S2. Measurements of Hg^{2+} spiked tap water and lake water

Samples	Hg^{2+}(nM) (n=3)		Recovery (%)
	spiked	detected	
Tap water	5	4.92 ±0.09	98.4
	20	21.6 ±0.79	108.1
	80	80.4 ± 1.92	100.5
Lake water	5	4.91 ±0.12	98.2
	20	19.2 ± 1.09	96.3
	80	78.4 ± 1.92	98.2

2.3. MSNs characterization

As shown in Fig S2, zeta potential of the newly prepared MSNs was -18.5 mV. A positive zeta potential (+12.17mV) was acquired when APTES was modified onto the MSNs, indicating the successful modification of APTES. After wrapping DNA was assembled onto the aminated MSNs, the zeta potential became negative (-7.2 mV). TEM images of DNA-gated MSNs and XRD characterization of MSNs were showed in Fig S3 and Fig S4, respectively.

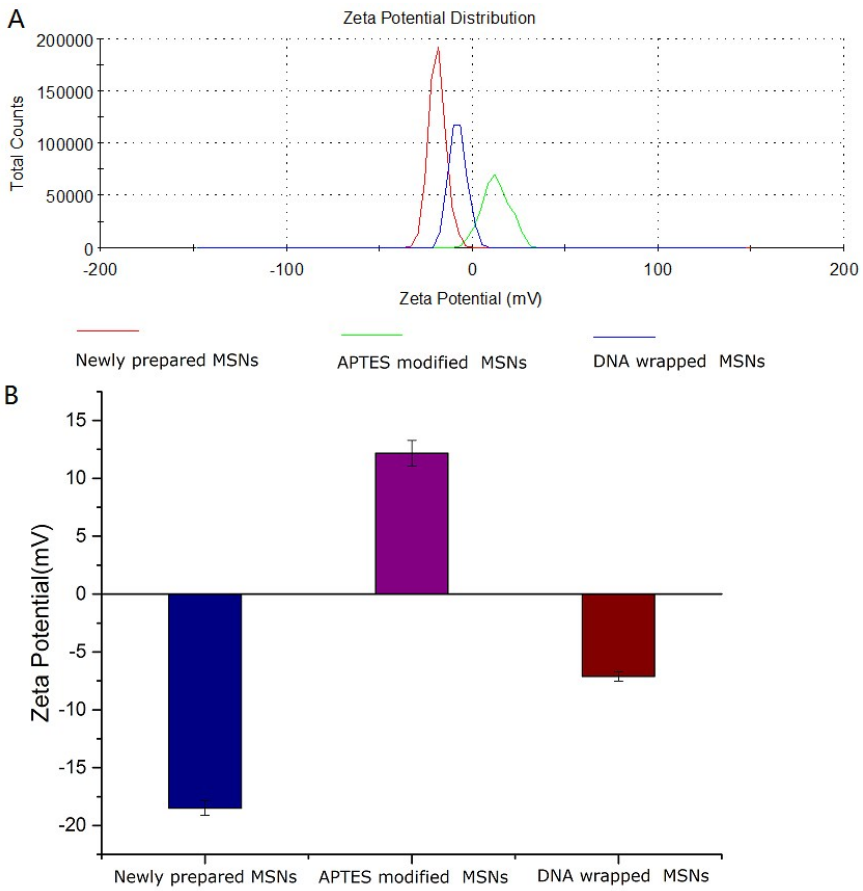

Fig. S2 Zeta potential of different types MSNs. (A) Zeta potential distribution of three types of MSNs. (B) Zeta potential value of three types of MSNs.

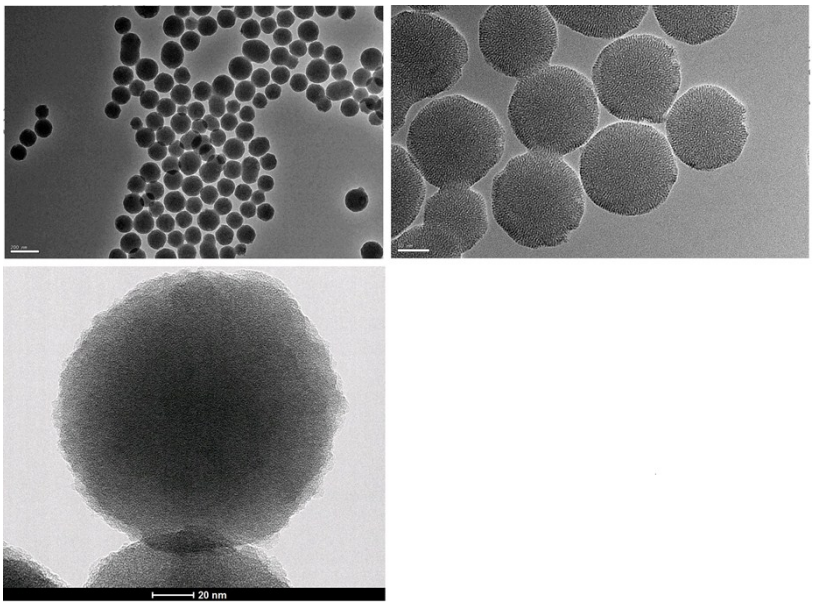

Fig. S3 TEM image of DNA-gated MSNs.

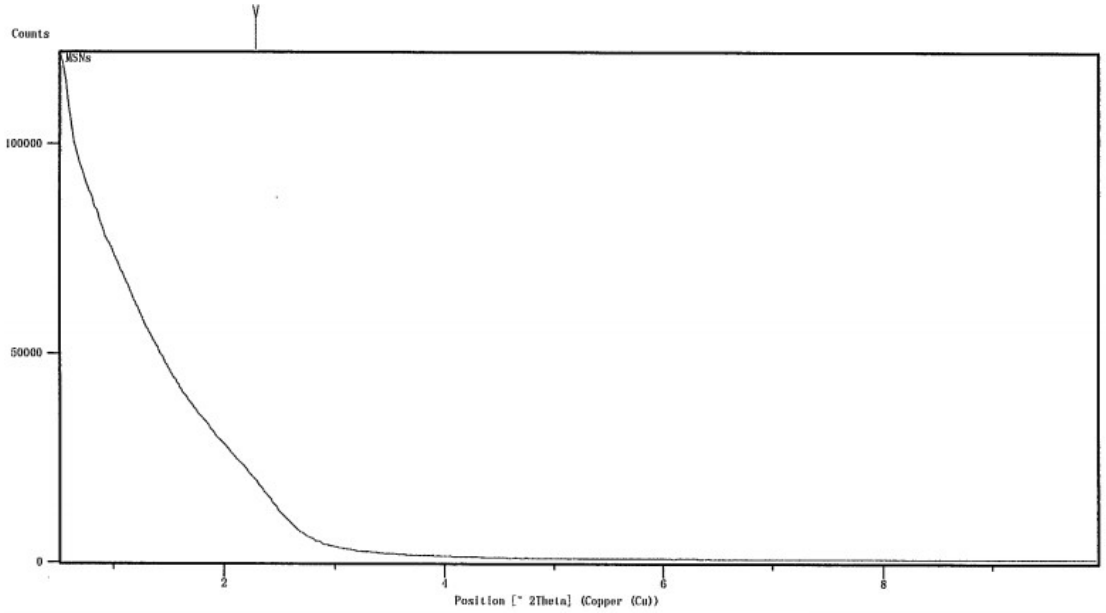

Fig. S4 XRD characterization of MSNs.

References

1. R. Qian, L. Ding and H. Ju, *Journal of the American Chemical Society*, 2013, **135**, 13282-13285.
2. L. Hou, C. Zhu, X. Wu, G. Chen and D. Tang, *Chemical communications*, 2014, **50**, 1441-1443.