Electronic Supplementary Material (ESI) for Analyst.

Electronic Supplementary Information

Visual / CVG-AFS / ICP-MS multi-mode and label-free detection of target nucleic acids based on selective cation exchange reaction and enzyme-free strand displacement amplification

Rui Dai,[a] Pingyue Hu,[a] Xiu Wang,[a] Shixin Wang,[a] Xinmei Song,[a] Ke Huang,*[a] and Piaopiao Chen*[b]

[a] College of Chemistry and Material Science, Sichuan Normal University, Chengdu, Sichuan, 610068, China

[b] Department of Laboratory Medicine, State Key Laboratory of Biotherapy and and Cancer Center, West China Hospital, Sichuan University and Collaborative Innovation Center for Biotherapy, Chengdu, Sichuan, 610041, China

*Corresponding authors. E-mails: chenpp0828@scu.edu.cn; huangke1987@126.com; huangke@sicnu.edu.cn.

Reagents. The quality of all reagents used in this work was at least analytical reagent grade. 18.2 MΩ cm resistivity pure water obtained from a Milli-Q water system (Chengdu Ultrapure Technology Co., Ltd., Chengdu, China) was used throughout this work. All oligonucleotides were obtained from Shanghai Sangon Biotechnology Co., Ltd (Shanghai, China). The sequences of these oligonucleotides are listed in Table 1. Stock solutions of the oligonucleotides were stored at -20 °C. $CdCl_2$, KBH_4, and $Na_3C_6H_5O_7 \cdot 2H_2O$ from Kelong Reagent Factory (Chengdu, China) and Na_2TeO_3 from Aladdin Reagent Co. (Shanghai, China) were used to prepare CdTe QDs. 3-mercaptopropionic acid (MPA) (Aladdin Reagent Co., Shanghai, China) was used as the capping agent for the QDs. High-purity hydrochloric acid (HCl) and NaOH were obtained from Kelong Reagent Factory (Chengdu, China). Human serum samples were provided by the Department of Laboratory Medicine, West China Hospital, Sichuan University (Chengdu, China). All working solutions were prepared with phosphate buffer saline (PBS) buffer (10 mM, 10 mM Mg^{2+}, pH 7.4).

Instrumentations. A commercial double-channel HG-AFS system (model AFS-2200, Beijing Ruili Instrument Co., Beijing, China) was employed for cadmium determination with high intensity cadmium hollow cathode lamps and a quartz gas-liquid separator (GLS). The concentration of Cd^{2+} in the solutions was determined using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 8900, USA). The fluorescence spectra were performed on a commercial F-7000 spectrometer (Hitachi, Japan). The absorption spectra were acquired on a UV-Vis spectrophotometer (lambda 950, PerkinElmer, USA). Temperature was controlled

with a RCT B S25 magnetic stirrer (IKA, Germany). And a MIX-25P shaker (Miou, Hangzhou, China) was used to mix the solution and a centrifuge (80-2B, Hunan Xinhai Instrument Co., Hunan China) was applied to centrifuge DNA and serum samples. Commercially available pre-packed sterile syringe filters (0.22 μm) was purchased from Tianjin experiment equipment Co. Ltd (Tianjin, China) was used to filter. High-resolution transmission electron microscope (HR-TEM) measurements of CdTe QDs were carried out by a Tecnai G2F20 STWIN TEM at an accelerating voltage of 200 kV (FEI Co., USA). The energy disperse spectroscopy (EDS) images of CdTe QDs + Hg^{2+} measurements were carried out with a field emission scanning electron microscope (SEM, JSM-7800F, JEOL, Japan). The survey scan and Hg images of the CdTe QDs + Hg^{2+} were carried out on a K-Alpha 1063 X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, England).

Synthesis of CdTe QDs. The CdTe QDs were prepared according to a previously reported one-pot synthetic method.[1-2] Briefly, 0.5 mmol of $CdCl_2$ and 0.20 g of trisodium citrate dehydrate were dissolved in 50 mL of water, followed by the instant addition of 52 μL of MPA. The pH of the solution was adjusted to 10.5, followed by the addition of 0.1 mmol Na_2TeO_3 and 50 mg KBH_4, the resulting solution was refluxed for 1 h. After the reaction, the color of the solution was red, which presented an intense red fluorescence under the UV lamp. The MPA-CdTe QDs were then kept at 4 ºC prior to use.

Table S1 Operational parameters of atomic fluorescence spectrometer (AFS)

Parameters	Value
Sampling time (s)	8
PMT high voltage (V)	-250
Carrier gas flow rate (mL/min)	400
Shielded gas flow rate (mL/min)	800
Observation height (mm)	8
Reading time (s)	7
Delayed time (s)	2
Cd hollow cathode lamp current (mA)	60
Pump rotation (r/min)	100

Table S2 Operational parameters of ICP-MS

Parameters	Value
Radiofrequency power	1550 W
Coolant argon gas flow rate	1 mL/min
Carrier (nebulizer) gas flow rate	15 mL/min
Auxiliary argon gas flow rate	1 mL/min
Scanning mode	Peak area
Dwelling time	40 s
Isotope monitored	Cd^{111}

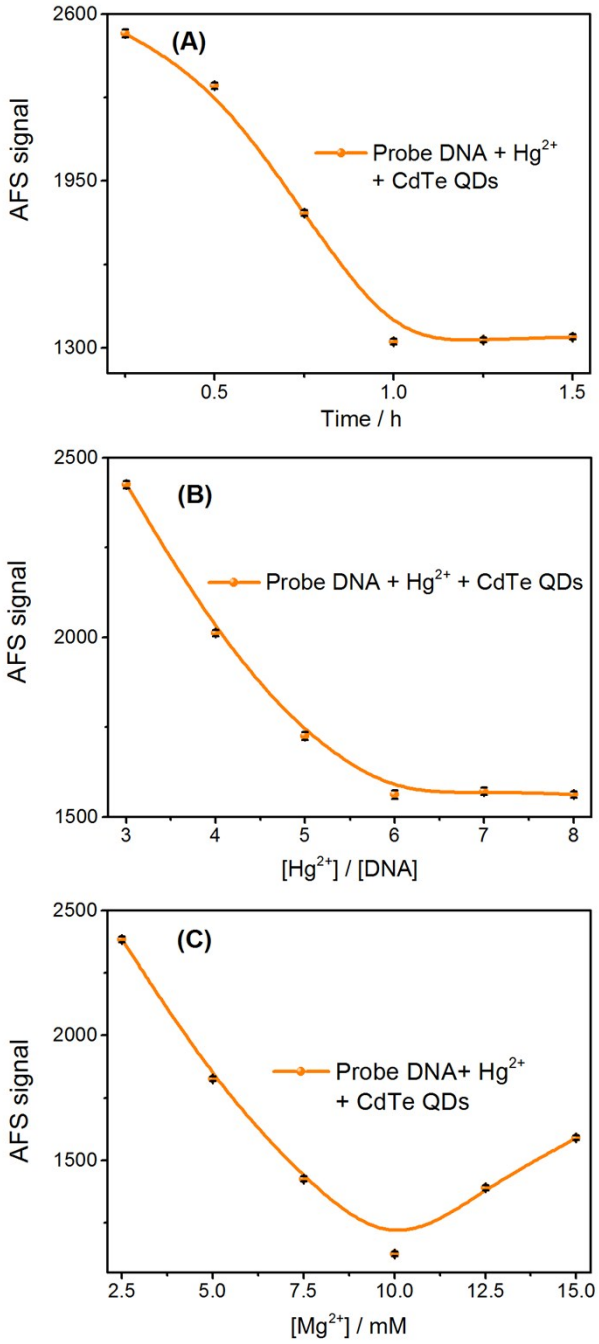

Fig. S1 Optimization of T-Hg^{2+}-T structure formation conditions. (A) Reaction time, (B) ratio of Hg^{2+} to probe DNA, and (C) Mg^{2+} concentration in PBS buffer solution. Error bars were estimated from three replicate measurements.

References

(S1) Huang, K.; Xu, K. L.; Tang, J.; Yang, L.; Zhou, J. R.; Hou, X. D.; Zheng, C. B. *Anal. Chem.* **2015**, 87, 6584-6591.

(S2) Sheng, Z. H.; Han, H. Y.; Hu, X. F.; Chi, C. *Dalton. Trans.* **2010**, 39, 7017-7020.