

Aptameric SERS sensor for Hg^{2+} analysis using silver nanoparticles

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Abstract

Aptamer–silver nanoparticles (AgNPs) based surface-enhanced Raman scattering (SERS) sensor has been developed for Hg^{2+} detection by employing the structure-switching aptamer in the presence of spermine. This simple method shows excellent sensitivity and selectivity owing to the sensitive SERS detection technique and high specificity of aptamer for binding Hg^{2+} .

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Keywords: Aptamer; AgNPs; SERS; Hg^{2+}

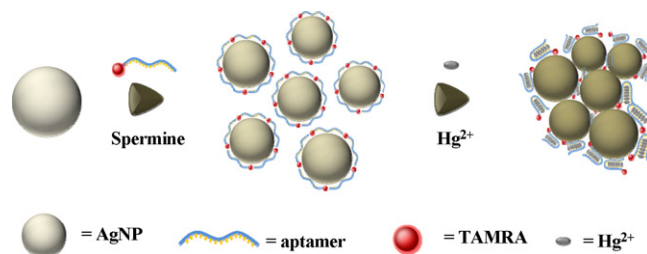
Owing to the resulting adverse effect on the ecosystem and the human beings [1], routine detection of Hg^{2+} is of importance for environmental monitoring and evaluation of safety of aquatically derived food supplies. Recently, thymidine (T)-containing aptamers constructed for Hg^{2+} sensors have attracted increasing interests of environmental analyst. Based on T– Hg^{2+} –T coordination [2] and simultaneous conformation change of aptamers, the Hg^{2+} sensing probes change the color and/or fluorescence intensity, which motivated various Hg^{2+} detection methods [3–6]. Surface-enhanced Raman scattering (SERS) is a well-known analytical method offering high sensitivity for biological and environmental detection [7]. To our best knowledge, however, there have been few studies on Hg^{2+} analysis by using SERS [8]. In this study, we described a novel method for sensitive and selective detection of Hg^{2+} using a SERS sensing platform based on a structure-switching aptamer. By applying Raman reporter-labeled aptamer, the AgNPs slightly aggregate in the presence of spermine. Upon the target addition, remarkable aggregation of AgNPs occurs and SERS signal is highly enhanced due to Hg^{2+} -induced structure-switching of aptamer, which opens a new way for Hg^{2+} recognition of high sensitivity and selectivity.

1. Experimental

SERS spectra were measured on a Renishaw 2000 Raman microscope system. A He–Ne laser operating at $\lambda = 633 \text{ nm}$ was used as the excitation source with a laser power of 12 mW and accumulation time of 10 s for each sample. The 5'-TAMRA-modified aptamer (5'-TAMRA-TTCTTTCTCCCTTGTTTGTT-3') was engineered for capturing target [9], where TAMRA acts as Raman reporter. AgNPs were synthesized at room temperature according to the previous report [10] with necessary modification. 5 mL of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (0.03 mol/L) and 1 mL of NaOH

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Scheme 1. Schematic diagram of an aptamer-AgNPs-based SERS sensor for Hg²⁺ detection.

(0.6 mol/L) were first dissolved in 84 mL of water. Then, 10 mL of AgNO₃ (0.01 mol/L) was dropwise added to the solution with strong stirring. The resulting solution was then continuously stirred for additional 1 h. The size of AgNPs was determined to be about 35 nm according to the TEM image. For the optimization of the sensing system, 50 nmol/L aptamer and 2.5 μmol/L spermine are successively used to treat AgNPs. 10 μL of Hg²⁺ solution was then added to 90 μL of the sensor solution and incubated for 3 min.

2. Results and discussion

Scheme 1 shows the aptamer-AgNP-based SERS sensing mechanism for Hg²⁺ analysis. As reported previously [11], unfolded aptamer can be adsorbed on the AuNP and protect AuNPs from salt-induced aggregation due to the Au-N coordination interaction. According to the fact that the affinity of Ag-N is higher than that of Au-N [12], we concluded that unfolded aptamer would be easily adsorbed on the AgNP and help to enhance the AgNP's stability, which agrees with our results. It is found that with more aptamer added, the silver colloids became more dispersed in the presence of spermine, which was used to aggregate and neutralize the negative-charged AgNPs. The aptamer-protected AgNPs display mild aggregation with a weak SERS signal in the presence of spermine (Fig. 1a). Upon the addition of Hg²⁺ and succedent formation of Hg²⁺-aptamer complexes in the solution, the conformation of aptamer changes to folded structure, thus reduces its capacity to protect AgNPs from aggregation in the presence of spermine. As a result, serious aggregation of AgNPs was observed and a significant increase of SERS intensity was obtained (Fig. 1a). These findings reveal the possibility of the sensing system for quantifying Hg²⁺ analytes.

The SERS signals were then measured upon the addition of Hg²⁺ at various concentrations. The band at 1651 cm⁻¹ was chosen as the maker band for TAMRA. Fig. 1b shows that the SERS intensity at 1651 cm⁻¹ monotonously increased with increasing Hg²⁺ concentration. The detection limit was determined to be 5 nmol/L, which indicated higher sensitivity of SERS-based sensor for Hg²⁺ compared to earlier studies [3–6].

Other popular metal ions (e.g., Ca²⁺, Zn²⁺, Fe²⁺, Cu²⁺, Cd²⁺, Pb²⁺) at same amount were also introduced to investigate the selectivity of the proposed sensing system. Interestingly and importantly, all the metal ions brought slight effects on the SERS signal of the SERS probe except Hg²⁺ as shown in Fig. 2, which demonstrated the high

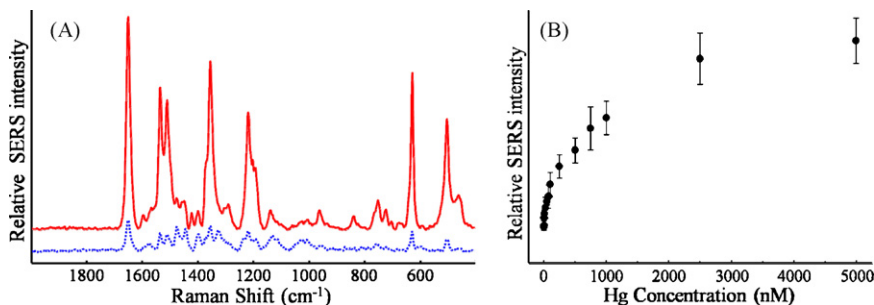


Fig. 1. (a) SERS spectra of the aptamer-AgNPs-based probe in absence (bottom) and presence (top) of Hg²⁺ ions (5.0 μmol/L). (b) Relative SERS intensity of TAMRA at 1651 cm⁻¹ vs various concentrations (nmol/L) of Hg²⁺ ions (from top to bottom: 5000, 2500, 1000, 750, 500, 250, 100, 75, 50, 25, 10, 7.5, 5.0 and 0, respectively.) The error bars denote the standard deviations of four measurements.

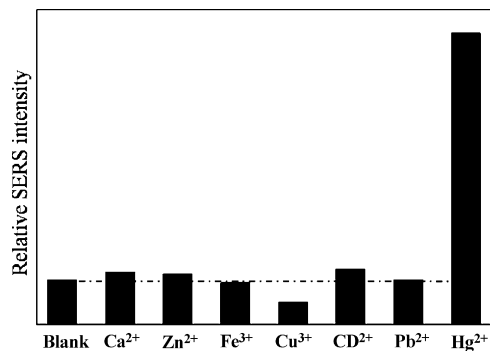


Fig. 2. Responses of SERS intensity of TAMRA at 1651 cm^{-1} to various metal ions at $5.0\text{ }\mu\text{mol/L}$.

selectivity of the sensing system for Hg^{2+} . The high selectivity is thought to result from the specific recognition of aptamer to Hg^{2+} .

In summary, highly sensitive analysis of Hg^{2+} has been achieved by using the aptamer–AgNPs-based SERS sensor. The significant SERS signal enhancement is almost specific for Hg^{2+} among various metal ions using the sensing system. Moreover, this method for the detection of Hg^{2+} is quite simple and timesaving. These advantages will promote this sensing system to find practical applications in the future.

Acknowledgments

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