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A facile aptamer-regulating gold nanoplasmonic SERS detection strategy for trace lead ions

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ABSTRACT

The as-prepared gold nanoparticle (AuNP) exhibited strong catalysis of the nanoreaction between H_2O_2 and $HAuCl_4$ to form gold nanoparticles (GNP) with nanoplasmonic surface-enhanced Raman scattering (SERS) at 1614 cm^{-1}, in the presence of Victoria blue B (VBB) molecular probes. Upon addition of the Pb^{2+} aptamer, it adsorb on AuNP surface to inhibit the its nanocatalysis, and the SERS, surface plasmon resonance (SPR) absorption and resonance Rayleigh scattering (RRS) decreased due to the redox product of GNP nanoplasmonic effect decreasing. When Pb^{2+} was added, the aptamer combined with it to form a very stable G-quadruplex and free AuNPs, which lead to the catalysis recovering, and the absorption, RRS and SERS intensity enhanced linearly. Hereby, a new and simple, sensitive and selective gold nanoplasmonic SERS platform was established for Pb^{2+}, based on the aptamer-regulating GNP nanoplasmonic SPR effect.

1. Introduction

Aptamer is an artificially selected short DNA/RNA chain that screened by SELEX in vitro [1,2]. It can be used as a molecular recognition probe with high selectivity, high affinity, easy marking, high stability and easy synthesis, and provides an efficient and rapid molecular recognition platform for life science and analytical chemistry. Recently, it was combined with the novel optical properties of metal nanomaterials to develop a series of selective and sensitive molecular spectral analysis such as absorption, fluorescence and resonance Rayleigh scattering (RRS) [3–6]. In addition, nanomaterials also have strong catalysis [7–14] and have been applied in analytical chemistry, one is used nanoparticle as catalyst for molecular reactions, another is used nanoparticle as catalyst for nanoparticle reaction that produced particles with nanoplasmonic effect such as SPR absorption, RRS and SERS. For the past few years, our group focused on the nanocatalytic RRS methods, combining the RRS effect of Cu(II)-N_2H_4 and $HAuCl_4$-vitamin C nanoparticle reaction with aptamer nanoprobe, some highly sensitive and selective RRS methods have been developed [15,16]. However, these methods need the as-prepared nanoprobes and its aggregation, and the process was complex.

One of the most powerful direct applications of nanoplasmon is SERS effect, it create a highly sensitive spectral method at molecular level [17,18]. In recent years, with the development of nanomaterial preparation technology, more and more nanomaterials have been utilized as SERS substrate for the food, environmental and clinical analysis [19,20]. To enhance the sensitivity and selectivity, SERS was combined with enzyme, immune and aptamer. Maher group [21] prepared the modified-AuNP with strong SERS effect, to detect 0.01 nM bioenzyme, based on the catalysis. Several aptamer-based SERS methods have been reported, with high sensitivity and selectivity [22,23]. Ye [23] used ssDNA to conjugate AuNP which exhibited a strong SERS signal in the presence of rhodamine 6G. Upon addion of As^{3+}, it bond with ssDNA that caused the SERS decreasing, and 0.288-23.04 ng/mL As^{3+} can be detected. Several nanocatalytic SERS quantitative analysis methods have been reported, with high sensitivity. Wen et al. [24] coupled the peptide, nanosilver aggregation and nanocatalysis to analysis of 0.05–10 ng/mL human chorionic gonadotropin. Ouyang et al. [25] reported a SERS method for detection of 0.013–0.5 μmol/L Hg(II), based on its inhabition of nanogold catalysis. Li et al. [26] developed a sensitive SERS quantitative analysis method for Cu(II),

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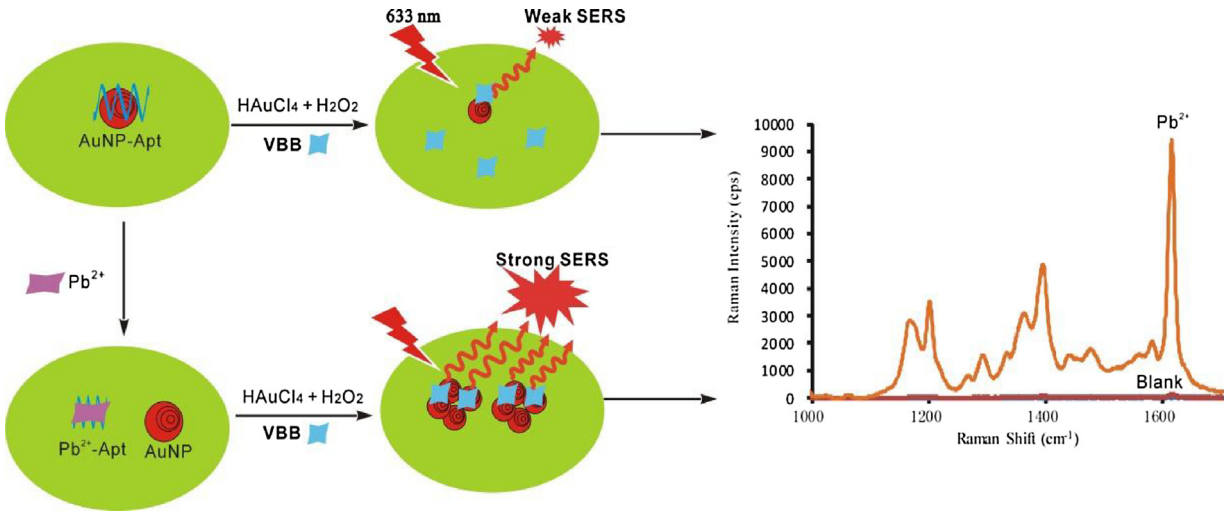

Fig. 1. Principle of the aptamer adjusting AuNP catalysis-SERS detection of Pb^{2+}.

combined its catalytic molecular reaction with AuNP aggregations. In the above methods, some were related to the macromolecular modification of noble metal nanoparticles, and some of them need nanoparticle aggregation. To overcome the above problems, we try to coupling amplify signal of nanocatalytic particle reaction with selective aptamer-regulating to develop facile, highly sensitive and selective nanoplasmonic SERS methods for trace targets such as lead ion.

Lead ion is a typical heavy metal pollutant, can exist in the environment for a long time and enriched through the food chain that threaten human health [27]. Therefore, the determination has been of necessary. To date, several methods have been reported for the determination of Pb^{2+}, such as inductively coupled plasma atomic emission spectrometry (ICP-AES) [28], absorption spectrometry [29,30], fluorescent spectrometry [31,32], mass-spectrometry [33], electrochemical method [34,35], RRS [6] and SERS [36,37]. To improve the selectivity and sensitivity, the aptamer methods were developed for Pb^{2+}. Zhao et al. [32] prepared graphene quantum dots-aptamer probe for Pb^{2+}, 9.9–435 nM Pb^{2+} can be determined by fluorescence method. However, it needed to prepare molecule probe with complexity operation. In this paper, we proposed a rapid, sensitive and selective SERS analysis platform for detection of Pb^{2+}, based on the aptamer-regulating AuNP catalytic particle reaction of $HAuCl_4$-H_2O_2.

2. Experimental

2.1. Apparatus and reagents

A model of DXR smart Raman spectrometer (Thermo Fisher Company, USA) with a laser wavelength of 633 nm and power of 2.5 mW and slit of 25 μm, a model of the Cary Eclipse fluorescence spectrometer (Varian Company, USA), a model of the TU-1901 double-beam UV–vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China), a model of FEI 200 FEG field emission scanning electron microscope (Dutch Philips, Holand), and a model of C-MAG HS7 incubation magnetic stirrer (IKA Company, Germany) were used.

Pb^{2+} aptamer with sequence of 5′-GGTTGGTGTGGTGGTTGGTGTTGG-3′ (PbApt, Biological Technology Co., Ltd., Shanghai, China), 1.0% $HAuCl_4$ (National Pharmaceutical Group Chemical Reagents Company, China), 1.0% sodium citrate, 0.01 mol/L HCl, 0.3% H_2O_2 (0.1 mol/L) were prepared, a 10^{-3} mol/L Victoria blue B (VBB) was prepared as follows, 0.025 g VBB was dissolved in 5.0 mL ethanol, and diluted to 50 mL with water.

Preparation of gold nanosol (AuNP): 50 mL of water was added into a flask and stirred to boil. Then 0.5 mL of 1% $HAuCl_4$ and 3.5 mL of 1% trisodium citrate were added rapidly into the boiling water successively. After boiling for 10 min with stirring, the sol color changed from colorless to wine red. The mixture was continuously stirred at room temperature and then diluted to 50 mL. The concentration was 58.0 μg/mL Au in size of 10 nm. And the 30 nm, 60 nm, 95 nm AuNPs were prepared by changed the amount of trisodium citrate. All reagents were of analytical grade, and the water was doubly distilled.

2.2. Procedure

A 10 μL of 0.15 μmol/L PbApt and a certain amount of Pb^{2+} were added into a 5 mL calibrated tube, and mixed well. After 10 min, 100 μL 8.4 μmol/L AuNP, 100 μL of 0.1% $HAuCl_4$, 20 μL of 0.01 M HCl and 20 μL of 0.3% (0.1 mol/L) H_2O_2 were added in turn, mixed well and diluted to 1.5 mL. The mixture was heated at 50 °C water bath for 11 min before it was cooled to room temperature with ice water. A 50 μL of 1.0×10^{-5} mol/L VBB was added and mixed well. The mixture was transferred into a 1 cm quartz cell. The SERS spectrum was recorded. The SERS intensity at 1614 cm^{-1} (I) and a blank (I_0) without Pb^{2+} were recorded, and a value of $\Delta I = I - I_0$ was calculated.

3. Results and discussion

3.1. Principle

Under the chosen conditions, the redox reaction of $HAuCl_4$-H_2O_2 was slow. When AuNP nanozyme was added into the reaction system, both oxidant of $HAuCl_4$ and reductant of H_2O_2 adsorb on the nanosurfaces, Au^{3+} was reduced to Au^+ and Au^0 by reductant. In which the surface electrons on AuNPs speed up the redox electron-transfer to form GNPs. The catalysis enhanced with the increasing of its concentration that resulted in formation of more products gold nanoparticles (GNP). Upon addition of VBB molecular probes, it exhibited a strong SERS effect at 1614 cm^{-1} that linearly enhanced with the AuNP concentration increasing. When aptamer was added, it wrapped on the AuNP nanozyme surface to form AuNP/PbApt to block the nanozyme catalysis, and the SERS intensity weakened. In the presence of Pb^{2+}, AuNP was released due to the Pb^{2+} spe-