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RESEARCH PAPER

Detection of Lead Ions in Water Based on the Surface Energy Transfer between Gold Nanoparticles and Fluorescent Dyes

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Abstract: In this paper, a sensitive method for the detection of lead ions in aqueous solution based on the surface energy transfer between gold nanoparticles and fluorescent dyes was established. The fluorescein-modified thrombin aptamer (5'-FAM-GGTTGGTGTGGTTGG-3') could be selectively transformed to G-quadruplex structure in the presence of lead ions. The conformational change of the aptamer could alter the distance between the energy donor of fluorescent dyes and the energy receptor of gold nanoparticles, resulting in an enhanced fluorescence intensity. The fluorescence recovery efficiency (F/F_0) was proportional to the concentration of lead ions in the range of 12.5–100 nM. The linear regression equation was $y = 0.910 + 0.007c$ ($R^2 = 0.997$) with the limit of detection (3σ) of 10 nM. The proposed method was applied to the determination of lead ions in tap water with satisfactory results.

Key Words: Aptamer; G-quadruplex; Gold nanoparticles; Surface energy transfer; Lead ions

1 Introduction

Nanomaterials surface energy transfer (NSET) has been extensively applied in analytical chemistry and biological chemistry researches, such as tracing DNA, measuring conformational changes of proteins, identifying intermediate of DNA folding, monitoring the interaction between DNA and metal ions, as well as detecting the important biological molecules associated with diseases[1–4]. Essentially, the mechanism of NSET is dipole-dipole interaction. The NSET differs from fluorescence resonance energy transfer (FRET), where the energy acceptor is the surface of nanoparticles that has a geometrically isotropic distribution of dipole vectors to accept energy from the donor. This arrangement increases the efficiency of energy transfer of NSET over that of FRET, and renders NSET with two important features[5,6]: (1) The same nanoparticle can quench the fluorescence emission from visible to near infrared region; (2) The relationship between the efficiency of energy transfer and the distance is changed from $1/R^6$ to $1/R^4$, which makes the measurable distance of NSET (about 15 nm) nearly doubled in comparison to FRET (about 9 nm)[6].

Lead ion, as a widespread heavy metal pollutant in environment, can cause the human kidney damage and mental retardation[7]. Therefore, it is very necessary to develop a simple and sensitive assay to real-time sensing of lead ions. Currently, DNAzyme sensors are widely used to detect lead ion in water[8–14] owing to its high sensitivity and selectivity. For example, Lu and others established a series of colorimetric assays[10–12] and FRET methods[13] for the determination of lead ions based on a lead-specific DNAzyme. The lead-specific DNAzyme was composed of an enzyme strand and a substrate strand. In the presence of Pb^{2+}, the enzyme strand could catalyze the cleavage of the substrate strand. This property was often utilized to control the transformations between dispersed and aggregated nanoparticles or the degree of FRET between donor and acceptor by the way of target recognition of DNAzmye. The

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sensitivity and selectivity of these methods were quite good, but strict reaction conditions were required for DNAzyme to generate specific hydrolysis cleavage, making the detection process more complicated.

It was reported that lead ions (r = 1.29 Å) could induce the G-rich oligonucleotides to form a stable G-quadruplex structure because of its suitable ionic radius to the cavity of G-quadruplex structure and strong coordination with nucleic acid bases[15]. It was found that thrombin-binding aptamer (TBA, 5'-GGTTGGTGTGGTTGG-3') could selectively transfer to G-quadruplex structure upon binding with lead ions [16]. In this work, the fluorescent dye carboxyfluorescein (FAM) modified at the 5' end of TBA as an energy donor was employed, citrate-stabilized spherical gold nanoparticle as an energy acceptor, to establish a NSET analysis of lead ions in aqueous solutions. The conformation of DNA strand would change from a random coil to G-quadruplex structure upon binding lead ions. Because the single-stranded and G-quadruplex (or double-stranded) structures have different propensities to adsorb on gold nanoparticles (AuNPs) in colloidal solution[17], the folding process affected by the concentration of lead ions could change the distance between the gold nanoparticles and the dye molecules. So the efficiency of energy transfer would be different, and a change of the fluorescence intensity could be observed. Thus, a simple and sensitive quantitative detection of lead ions by monitoring the fluorescence intensity in solution was achieved.

2 Experimental

2.1 Instruments and reagents

The fluorescence spectra were obtained with a Hitachi F-2500 spectrofluorometer (Hitachi, Tokyo, Japan) by scanning the emission monochromators from 500 to 600 nm with an excitation wavelength at 485 nm. A pHS-3C digital pH meter (Chengdu Century Ark Technology Co.Ltd, Chengdu, China) was used to measure the pH values of the aqueous solutions, and a QL-901 vortex mixer (Haimen Qilinbei'er Instrumental Ltd., Haimen, China) was employed to blend the solutions. A 90-1 magnetic stirrer (Shanghai Jingke Industry Co., Ltd.) was used for heating and stirring during the preparation of gold nanoparticles.

Hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4 \cdot 4H_2O$), trisodium citrate and lead nitrate were commercially obtained from Sinopharm Group Chemical Regent Co., Ltd. (Shanghai, China), Shanghai Chemical Reagent Inc. (Shanghai, China) and Chuandong Chemical Group Co., Ltd. (Chongqing, China), respectively. The carboxy-fluorescein-modified thrombin aptamer (FAM-TBA) (5'-FAM-GGTTGGTGTGGT TGG-3') were purchased from Sangon Biotechology Inc. (Shanghai, China). After centrifuged at 5000 rpm for 5 min, this DNA product was dissolved in 1 mL newly boiled and cooled ultrapure water and stored at 4 °C. Ultrapure water (18.2 MΩ cm, LD-50G-E Lidi ultra pure waters system, Chongqing) was used throughout. Tris-acetic acid (Tris-HAc) buffer solution was used to control the pH values. All other reagents in this experiment were of analytical reagent grade and used without further purification.

2.2 Experiment methods

2.2.1 Preparation of AuNPs

The citrate-capped AuNPs were prepared according to literature[18] with slight modification. Briefly, 1.0 mL of 5.0% trisodium citrate solution was rapidly added into 49 mL boiling solution containing 1 mL 1% $HAuCl_4$ under vigorous stirring. The solution was boiled for another 5 min until its color changed from blue into red. Then the solution was cooled down to room temperature with continuous stirring. The concentration of AuNPs was estimated to be *ca*. 5.0 nM, which was calculated from its absorbance at 520 nm according to Lambert-Beer's law, using the extinction coefficient of 2.7×10^8 M^{-1} cm^{-1} for 13 nm AuNPs[19]. All glassware prior to be used in the preparation procedures were thoroughly cleaned with chloroazotic acid and water.

2.2.2 Detection of lead ions

The DNA solutions were first heated at 88 °C for 5 min to dissociate any intermolecular interaction[20], and cooled to room temperature with ice water. Then, appropriate amount of lead nitrate and 5.0 mM (pH 7.4) Tris-HAc buffer were added into the DNA solution, and incubated for 15 min to allow the formation of the quadruplex structures stabilized by Pb^{2+}. After that, 2.0 nM of AuNPs were added into the solution and incubated for another 5 min, and then the fluorescence spectra were recorded.

3 Results and discussion

3.1 Principle of Pb^{2+} detection via NSET

Figure 1 shows the sensing strategy of the FAM-TBA probe for the detection of Pb^{2+} ions via NSET. Specifically, FAM-TBA was used as the energy donor, and the unmodified and negatively charged AuNPs were used as the energy acceptor. When TBA adopted the random coil conformation, the exposed bases had a strong affinity to AuNPs because of the formation of Au-N covalent bond, which facilitated the adsorption of TBA on the surface of AuNPs[17]. Upon the adsorption of TBA to AuNPs, the FAM tagged on TBA came close to the AuNPs, and the energy transfer from FAM to the surface of AuNPs occurred, along with the quenching of fluorescence of FAM. With the addition of lead ions, the TBA