Sensors and Actuators B 212 (2015) 481–486

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Gold nanoparticle-based colorimetric detection of mercury ion via coordination chemistry

Jianjun Du*, Zhenkuan Wang, Jiangli Fan, Xiaojun Peng

State Key Laboratory of Fine Chemicals, Dalian University of Technology, 2 Linggong Road, Dalian 116024, PR China

ARTICLE INFO

Article history:
Received 15 November 2014
Received in revised form 27 January 2015
Accepted 27 January 2015
Available online 16 February 2015

Keywords:
Colorimetric assay
Gold nanoparticle
Coordination chemistry
Thymine derivative
Mercury ion

ABSTRACT

A simple, fast, and convenient colorimetric detection of Hg^{2+} in aqueous media was presented based on the selective binding capability of thymine derivative (**N-T**) toward Hg^{2+}. **N-T** decorated AuNPs solution was stable in red color, while the presence of Hg^{2+} induces significant aggregation of AuNPs along with red-to-blue color changes. Therefore, Hg^{2+} content in real water samples can be qualitatively detected by our naked eyes; meanwhile, good linear relationship of Hg^{2+} along with $A_{650\ nm/520\ nm}$ values could be obtained for its quantitative determination. Furthermore, our system shows excellent selectivity to mercury ions against any other tested metal ions and anions, and good sensitivity with LOD of 0.8 nM in real water samples.

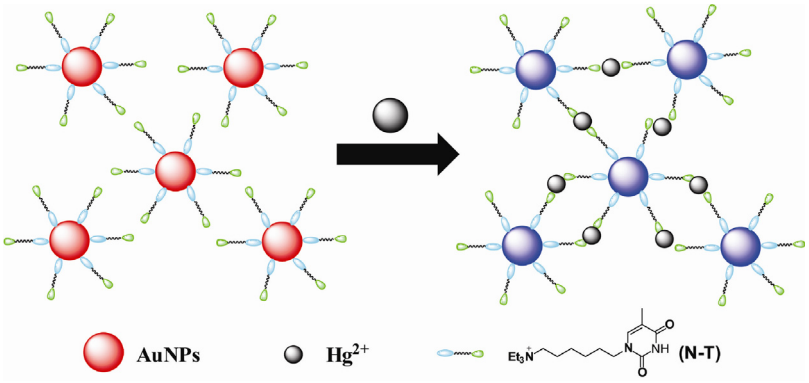
1. Introduction

Mercury is one of the most useful metal elements in paints, mining, pesticides, ammunition factory and so on [1,2], which meanwhile lead to the widespread mercuric contaminations [3]. Increasing concerns over mercury exposure and its deleterious effects on public health and environment safety promote developing fast, specific, low-cost, and efficient tools as well as tactics for mercury ion detection [4]. Compared with complicated instrument-based methods, gold nanoparticles (AuNPs)-based colorimetric assay [5–8] has drawn increasing attention due to its greater absorption extinction coefficient, tunable surface plasmon resonances (SPRs) and naked eye-distinguishable readouts, which make it one of the most suitable strategies for practical applications [9,10]. Therefore, by adjustable external stimulations [11–13], AuNPs-based assay is applied in the study of protein [14–16], enzyme [17–19], DNA [20,21], biomolecules [22,23], and ions [24–27], showing excellent sensitivity, accuracy, and fast colorimetric changes [28,29]. Recently, dsDNA [30–33] (with thymine–thymine mismatch) and ssDNA [34,35] (with plenty of thymine) have been designed and synthesized for colorimetric detection of Hg^{2+} based on the specific binding capability of thymine to Hg^{2+} [36,37]. Then, to avoid the synthesis of DNA and accurate control in following detection (such as the melting temperature of dsDNA), functional molecules have been presented based on the coordination chemistry and mild redox reaction [38–51]. Nevertheless, some systems, such as some acid-AuNPs systems, suffer from interference of other metal ions (such as Pb^{2+} and Cd^{2+}), wherein mask agents have to be introduced, while for redox-based system, Ag^{+} is clearly one of the biggest threats. Therefore, the main challenge is to develop a selective, sensitive, and stable system that can avoid these consequences.

In this context, with the above motivations, intense endeavor has been dedicated to presenting a fast, sensitive, and stable AuNPs system for Hg^{2+} sensing especially with good selectivity and anti-interference capability. Thymine has been proved to be one of the best ligands for selectively catching Hg^{2+} [52–54], though poor solubility in neutral aqueous media could affect its sensing capability. In this work, we thereby introduce a hydrophilic group to endow thymine better performance for Hg^{2+} detection in aqueous samples. As a proof-of-concept, we synthesized and applied a thymine derivative modified with quaternary ammonium salt (**N-T**, as shown in Scheme 1), which was introduced not only to increase the water solubility but also to act as an anchor by electrostatic effect when functionalized on gold surface. The **N-T** was synthesized according to the published literatures [55,56]. Scheme 1 illustrates the working principle of our colorimetric system. The **N-T** decorated AuNPs (13 nm) solution displays red color with absorption peak at about 520 nm, while the presence of Hg^{2+} induces fast aggregation of AuNPs along with significant

* Corresponding author. Tel.: +86 41184986327.
E-mail address: dujj@dlut.edu.cn (J. Du).

http://dx.doi.org/10.1016/j.snb.2015.01.110
0925-4005/



Scheme 1. Schematic illustration of **N-T**/AuNPs-based colorimetric detection of Hg^{2+}.

red-to-blue color change. Thanks to respective functions of thymine and quaternary ammonium, this system realizes fast, sensitive, and selective detection of Hg^{2+} in aqueous media without masking agent. And the limit of detection (LOD) reached as low as 0.8 nM in real water systems, which endows our system's capability of distinguishing safe water from Hg^{2+} polluted samples.

2. Experimental

2.1. Chemicals

Gold(III) chloride trihydrate (99.9+%) was purchased from Sigma–Aldrich. The solutions of anions and metal ions were prepared from NaCl, $MgCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $ZnCl_2$, $CdCl_2$, $CaCl_2$, $BaCl_2$, $CuCl_2{\cdot}2H_2O$, $PbCl_2$, $NiCl_2$, $CrCl_3$, $MnSO_4$, KBr, $AgNO_3$, $HgCl_2$, $FeCl_3{\cdot}6H_2O$, NaSCN, Na_2SO_4, $NaClO_4{\cdot}H_2O$, KI, NaOAc, KBr, KCl, $Na_2P_2O_7$, $K_2HPO_4{\cdot}3H_2O$, Na_3PO_4, $NaNO_3$, $NaNO_2$, and Na_2CO_3, by separately dissolving each metal ion in distilled water. All other chemicals were supplied by Aladdin Reagent Company and Energy Chemical Reagent Company, and were used as received.

2.2. Instruments

^1H NMR spectra were recorded on a VARIAN INOVA-400 spectrometer with chemical shifts (δ) reported as ppm (in $CDCl_3$, TMS as the internal standard). Mass spectrometry data were obtained with an HP1100LC/MSD mass spectrometer and an LC/Q-TOF MS spectrometer. AuNPs were characterized by transmission electron microscopy (TEM, T20) at 200 kV. Absorption spectra were measured on a Lambda 35 UV/Vis spectrophotometer (Perkin Elmer). All pH measurements were made with a Model PHS-3C meter. The zeta potentials of AuNPs before and after modification by **N-T** were measured by ZETASIZER nano series Nano-ZS90.

2.3. Synthetic procedures

The synthesis of **N-T** followed the general route as shown in Fig. S1.

Synthesis of ***1***: Potassium carbonate (3.03 g, 3.00 mmol) was added into a suspension of thymine (0.93 g, 1.00 mmol) in dry DMF (20 mL), and the mixture was heated at 40 °C for 1 h. After the mixture was cooled to room temperature, 1,6-dibromohexane (5.41 g, 3.00 mmol) was added, and the resulting mixture was heated at 40 °C for 3 h whereupon it was evaporated. The crude was treated with CH_2Cl_2 (150 mL) and filtered. The filtrate was purified by silica gel column chromatography (EtOAc/hexane) to afford **1** (704 mg, 33.4%). ^1H NMR (400 MHz, $CDCl_3$), δ: 8.93 (s, 1H), 6.98 (s, 1H), 3.70 (t, J = 8 Hz, 2H), 3.41 (t, J = 8 Hz, 2H), 1.98 (t, 3H), 1.87 (m, 2H), 1.70 (m, 2H), 1.50 (m, 2H), 1.36 (m, 2H); MS: ($C_{11}H_{17}BrN_2O_2$ $[M+H]^+$) m/z 289.11.

Synthesis of **N-T**: **1** (156 mg, 0.57 mmol) and a spot of KI in dry DMF (5 mL) were added into a flask (50 ml) in ice-bar. The triethylamine (818 mg, 8.1 mmol) was then added. The ice bath was then removed, and the solution was stirred at 80 °C for 2 h whereupon it was evaporated. The crude was purified by neutral alumina column chromatography (CH_2Cl_2/CH_3OH) to afford **N-T** (85 mg, 50.3%). ^1H NMR (400 MHz, $CDCl_3$), δ: 8.63 (s, 1H), 7.36 (s, 1H), 3.76 (t, J = 8 Hz, 2H), 3.48 (q, J = 8 Hz, 6H), 3.39 (t, J = 8 Hz, 2H), 1.95 (s, 3H), 1.78 (m, 4H), 1.50 (m, 4H), 1.40 (t, J = 8 Hz, 9H); TOF MS: m/z calcd for $C_{17}H_{32}N_3O_2^+$ $[M]^+$: 310.2489, found: 310.2496.

Synthesis 13 nm AuNPs: AuNPs (13 nm) was prepared by sodium citrate reduction of a $HAuCl_4$ solution as described in the literature [57].

2.4. Fabrication of *N-T*/AuNPs system

The AuNPs solution was centrifuged (10,000 rpm, 15 min) before the following modification. In order to stabilize the AuNPs system, Tween 20 was introduced as stabilizer, which can protect AuNPs from aggregation induced by interferents and the stimulus in the test environment. According to the control experiment, 1 ppm Tween 20 was proved optimal which was used in this work (Fig. S2).

And then quantitative **N-T** was added into Tween 20-protected AuNPs solution to simplify the fabrication of **N-T**/AuNPs system. When 5 μM **N-T** was added, the $A_{650\ nm/520\ nm}$ value reached to about 1.1 which exhibited best efficiency for mercury ion sensing (Fig. S3). Therefore, 5 μM **N-T** was the optimal concentration for the modification. After 10 min incubation, **N-T**/AuNPs solutions were ready for testing. The zeta potentials of −25.8 mV and −18.0 mV were obtained before and after functionalization of positive **N-T** on gold surface, which confirmed the surface charge changes upon **N-T** modification.

2.5. Pretreatment of real water samples

Both the tap water (collected from our lab) and natural drinking water (Nongfu spring) were selected for practical detection of Hg^{2+}. Standard solutions of varying Hg^{2+} concentrations (50–250 nM) were prepared from a concentrated stock solution with Hg^{2+} (0.5 mM) and were artificially added to the water samples. The pH value of these AuNP solutions was adjusted to 7.0. In the test, 500 μL **N-T**/AuNPs solution was added into 1000 μL water samples followed by UV–Vis spectra recording after 10 min incubation.