



A rapid and sensitive colorimetric assay method for Co^{2+} based on the modified Au nanoparticles (NPs): Understanding the involved interactions from experiments and simulations

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ABSTRACT

We previously reported a colorimetric assay method for Co^{2+} based on the thioglycolic acid (TGA) functionalized hexadecyl trimethyl ammonium bromide (CTAB) modified Au NPs. However, the detection limit of 3×10^{-7} M was still higher than that of the sanitary standard for drinking water (6.8×10^{-8} M). In addition, the interactions between the modifier and Au NPs, and between the modifier-Au NPs and Co^{2+} remain to be clarified and confirmed. Thus, in the present study, the modified Au NPs solution was dialyzed and its detection limit was optimized to be 5×10^{-10} M. The interactions between the modifier and Au NPs, and between the modifier-Au NPs and Co^{2+} were investigated in both experimental characterizations and theoretical calculations, consistently confirming that the Au NPs were modified by the negatively charged anions of $[\text{SCH}_2\text{CO}_2]^{2-}$ through Au–S bonds and Co^{2+} was recognized by the modifier-Au NPs through Co–O chelate bonds. The results of X-ray photoelectron spectroscopy (XPS) suggest that there were no chemical bonds formed between CTAB and Co^{2+} . Moreover, the colorimetric assay of Co^{2+} using the modified Au NPs has been proved to be a rapid, very sensitive and highly selective method. The validation of the method was carried out by analysis of a certified reference material, GSBZ 50030-94.

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1. Introduction

Cobalt is one of the essential trace elements that humans and many other living creatures require for good health [1]. As part of Vitamin B12, cobalt can promote the formation of red blood cells [2]. However, cobalt also causes severe effects on human beings and animals arising from overexposure to the environmental water polluted by Co^{2+} [3–5]. The toxicological effects of Co^{2+} on human beings may lead to loss of appetite, flushing and vasodilatation, even terrible diseases such as anemia and cardiomyopathy [6,7]. Thus, the determination of trace amount of Co^{2+} in biological and environmental samples is very essential. Several methods have been used for Co^{2+} analysis, including inductively coupled plasma–atomic emission spectrometry (ICP–AES) [8], fluorescence techniques [9], fiber optic–linear array detection spectrophotometry (FO–LADS) [10], electrochemical approach [11,12], flame atomic absorption spectrometry (FAAS) [4,5,13] and spectrophotometry [14], etc. Without the aid of any advanced instruments, colorimetric methods can be convenient and easily monitored with the naked eyes. So the colorimetric methods have attracted considerable

attention in detection of toxic metal ions including Co^{2+} [15–19]. Yao et al. [15] and Maity and Govindaraju [16] applied the different colorimetric assay methods for Co^{2+} with the detection limit of 1×10^{-5} M and 1×10^{-6} M, respectively. Previously, we developed a colorimetric assay method for Co^{2+} based on the thioglycolic acid (TGA) functionalized hexadecyl trimethyl ammonium bromide (CTAB) modified Au NPs with the detection limit of 3×10^{-7} M [19]. All the reported limits of colorimetric detection of Co^{2+} are quite higher than the level of 6.8×10^{-8} M according to the sanitary standard for drinking water [21]. As a result, there is high demand for the development of highly sensitive methods to detect Co^{2+} . Moreover, up to date, all the researches on the interactions between the ligands and the detected ions/biological molecules still built on assumptions and conjecture [15–20].

Here, we developed a highly rapid and sensitive colorimetric assay method for Co^{2+} based on dialyzing the previous modified Au NPs solution [19] and its limit of colorimetric detection was optimized to be 5×10^{-10} M, which is much lower than previously reported data of 3×10^{-7} M [19] and even lower than the level of 6.8×10^{-8} M according to the sanitary standard for drinking water [21]. In addition, we extend our effort to investigate the interactions between the modifier and Au NPs, and between the modifier-Au NPs and Co^{2+} using the experimental means and density functional theory (DFT) calculations. Experimentally, dynamic

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light scattering (DLS) has been proved to be a powerful tool for determining small changes in the size and zeta potential of particles in solutions [22–24]. Moreover, DLS has been demonstrated to be sensitive in probing the interaction between molecules and Au NPs [22–24]. Herein, DLS was used to determine the changes both in the size and zeta potential of the Au NPs modified by 2-thioethanoate ($[\text{SCH}_2\text{CO}_2]^{2-}$), which were dissociated from TGA ($\text{HSCH}_2\text{CO}_2\text{H}$) in solution. Theoretically, the DFT calculation has proved to be a powerful tool for determining the structures and interaction mechanisms of molecules [25–28]. In particular, the DFT calculation has been used to explore the vibrational frequencies of molecules [25,26]. In the current work, the DFT calculations were used to determine the molecular structures of $[\text{AuSCH}_2\text{CO}_2]^-$ and $[\text{3AuSCH}_2\text{CO}_2 + \text{Co}]^-$ involved in the experiment, and simulate their vibrational frequencies compared with the experimental results. The corresponding vibrational spectra of Fourier transform infra-red spectroscopy (FT-IR) and DFT calculations consistently confirmed that the Au NPs were modified by $[\text{SCH}_2\text{CO}_2]^{2-}$ through Au-S bonds and Co^{2+} was recognized by the modifier-Au NPs through Co–O bonds, which were proved by XPS to be Co–O chelate bonds. The combination of experimental characterizations and theoretical calculations demonstrated the hypothetical mechanism in our previous work [19]. While there were no chemical bonds formed between CTAB and Co^{2+} .

In addition, the recognition time of Co^{2+} by modified Au NPs has been proved to be within 1 min, which is much less than the detection time (~ 3 h) of ICP-AES needed for the pre-concentration of trace Co^{2+} before analysis. The probe of modified Au NPs has very high specificity toward Co^{2+} both in freshwater and hypothetical seawater. The practicality of the modified Au NPs for analysis of Co^{2+} in real environmental water was demonstrated by the colorimetric assay with satisfactory results.

2. Experimental

2.1. Materials

Thioglycolic acid (TGA), LiCl, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were obtained from Aladdin-regent Co. Ltd (Shanghai, China). Sodium borohydride (NaBH_4), chloroauric acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), KCl, NaCl, AlCl_3 , FeCl_3 , ZnCl_2 , HgCl_2 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, CaCl_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, Na_2CO_3 , Na_3PO_4 , Na_2SO_4 , $\text{Na}_2\text{C}_2\text{O}_4$, $\text{Pb}(\text{NO}_3)_2$, lysine, threonine, cysteine, arginine, histidine and hexadecyl trimethyl ammonium bromide (CTAB) were obtained from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). The certified reference material GSBZ 50030-94 was obtained from Institute for Environmental Reference Materials of Ministry of Environmental Protection (Beijing, China). All of the chemicals were used without purification. Millipore-Q water was used throughout the experiment. All glassware were washed with aqua regia ($\text{HCl}/\text{HNO}_3 = 3:1$ (v/v). It is very strong corrosive!!!) and then cleaned with Milli-Q water.

2.2. Methods and characterization

X-ray powder diffraction (XRD) was performed using a Bruker D8 Advance/Discover diffractometer (Bruker Co. Ltd., Germany) with Cu $\text{K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Fourier transform infra-red spectroscopy (FT-IR) was performed using a Nicolet 6700 spectrometer. Dynamic light scattering (DLS) was performed using Zetasizer Nano ZS instrumentation (Malvern Instruments Ltd). Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) were performed using a Tencai F20 instrument and operated at 200 kV. UV–vis absorption spectra were

recorded in the range of 400–800 nm using a Lambda 950 UV–vis spectrophotometer from Perkin Elmer. X-ray photoelectron spectroscopy (XPS) was performed using an AXIS Ultra DLD instrument with Mg $\text{K}\alpha$ radiation as the X-ray source. The including inductively coupled plasma–atomic emission spectrometry (ICP-AES) data were recorded on an Optima 2100DV ICP instrument.

2.2.1. Preparation of the modified Au NPs

According to Murphy's method [29], Au NPs were prepared by reducing HAuCl_4 with NaBH_4 , and stabilized by CTAB. The synthetic Au NPs solution was centrifuged to remove CTAB and characterized by XRD. 100 μL of TGA ($\text{HSCH}_2\text{CO}_2\text{H}$) was added into 100 mL of the Au NPs solution without centrifugation, while the pH value of the mixed solution was controlled to be 8.0. The concentrations of TGA and Au NPs in the solution were controlled to be $\sim 1.3 \times 10^{-2} \text{ M}$ and $2.1 \times 10^{-4} \text{ M}$, respectively. After adding TGA for 0 min, 5 min, 20 min, 40 min, 60 min, 90 min, 120 min and 150 min, 12 mL of the mixed solution was centrifuged at 10,000 rpm for 10 min and characterized the particle size and zeta potential of the modified Au NPs using DLS, respectively. The modified Au NPs were then characterized by TEM and EDS.

2.2.2. Interference studies

The selective recognition of Co^{2+} by modified Au NPs in freshwater and hypothetical seawater was studied respectively. The selectivity for Co^{2+} in freshwater was investigated as follows: the representative metallic ions (Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Cr^{3+} , $\text{Cr}(\text{VI})$, Hg^{2+} , Pb^{2+} , Co^{2+}) (0.5 mL , $8 \times 10^{-5} \text{ M}$), anions (Cl^- , $\text{C}_2\text{O}_4^{2-}$, SO_4^{2-} , CO_3^{2-} , PO_4^{3-}) (0.5 mL , $8 \times 10^{-4} \text{ M}$) and amino acids (lysine, threonine, cysteine, arginine, histidine) (0.5 mL , $8 \times 10^{-5} \text{ M}$) were added into the modified Au NPs solutions (3.5 mL), respectively. Their color and UV–vis spectra were compared with the blank control group. The final concentrations of the tested metallic ions, anions and amino acids were 10^{-5} M , 10^{-4} M and 10^{-5} M , respectively.

The procedure for the selective recognition of Co^{2+} by modified Au NPs in hypothetical seawater is similar with that in freshwater, while the significant difference is that the NaCl concentration in hypothetical seawater was controlled to be 0.62 M, which is the highest concentration of NaCl in seawater.

2.2.3. The detection of Co^{2+} by modified Au NPs

For the detection of Co^{2+} , the modified Au NPs solutions ($\sim 2.1 \times 10^{-4} \text{ M}$) was dialyzed to remove the excess CTAB and TGA, and then mixed with the various concentrations of Co^{2+} ranging from 0 to $1 \times 10^{-4} \text{ M}$.

To probe the interactions between the modifier-Au NPs and Co^{2+} , 10 mL of different concentrations of Co^{2+} (0 , 2×10^{-4} and $2 \times 10^{-3} \text{ M}$) were added to 30 mL of the modifier-Au NPs solutions, respectively. The final concentrations of Co^{2+} in the modifier-Au NPs solutions were 0 , 5×10^{-5} and $5 \times 10^{-4} \text{ M}$, respectively. The mixtures without centrifugation were freeze-dried for 36 h and characterized by FT-IR and XPS.

2.3. Structure and frequency calculations

The geometry optimizations on the structures of $[\text{AuSCH}_2\text{CO}_2]^-$ and $[\text{SCH}_2\text{CO}_2]^{2-}$ were performed by means of DFT methods using the GAUSSIAN03 quantum chemistry package. The stable conformer of $[\text{3AuSCH}_2\text{CO}_2 + \text{Co}]^-$ was determined by optimizing the trial structures (~ 1000) obtained by adding Co^{2+} to the stable conformers of $[\text{AuSCH}_2\text{CO}_2]^-$ at different binding sites. In order to ascertain the structural accuracy and stability, the vibrational frequencies of the stable structures of $[\text{AuSCH}_2\text{CO}_2]^-$, $[\text{SCH}_2\text{CO}_2]^{2-}$ and $[\text{3AuSCH}_2\text{CO}_2 + \text{Co}]^-$ were calculated at the BHandHLYP/6-31G* level and compared with the experimental FT-IR spectra. We

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