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A submicromolar Cr(III) sensor with a complex of methionine using gold nanoparticles

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ABSTRACT

We report a combined approach for the detection of Cr(III) after the binding L-methionine (Met) and subsequent treatment with gold nanoparticles (AuNPs) by colorimetric, UV–vis absorption, and surface-enhanced Raman scattering (SERS). Both UV–vis and SERS led to a selective detection of Cr(III) at the submicromolar level. The absorbance values at 650 nm for Met–Cr(III)–AuNPs could be correlated quantitatively with the concentrations of the Cr(III) ion. The detection limit of Cr(III) was estimated be as low as 300 nM based on the absorbance measurements of the aggregated AuNPs at 650 nm. Environmental (distilled, tap, river, and sea) water samples with different ionic compositions were also tested to validate our method. After the binding the metal ion in aqueous solutions, the amino acid Met was found to be a sensitive and selective sensor for Cr(III) on the AuNPs in the water samples without interference from the other ions.

1. Introduction

Nanostructured materials have been extensively used in many analytical methods of metal ions in biological media [1]. Recent developments in methodolgies for the detection and quantitation of biological molecules in aqueous solutions, are now receiving much attention [2–5]. Raman spectroscopy is currently the method of choice for detection of trace ions. Surface-enhanced Raman spectroscopy (SERS) has recently been used to detect trace amounts of several toxic substances [6]. Ultra-sensitive detection of ions is feasible through the combination of aggregation-dependent noble metal nanoparticles (NPs) in the field of nanobioanalysis [7].

Trivalent chromium is used as a dietary supplement in the form of chromium polynicotinate and picolinate to enhance the activity of insulin [8,9]. In mammals, Cr(III) is an essential micronutrient and participates in the maintenance of effective carbohydrate metabolism by activating certain enzymes [10]. Chromium detection in water has usually required conventional approaches. Various analytical techniques have been employed for the quantification of chromium (III) [11–14].

Gold nanoparticles (AuNPs) and nanoclusters have been currently used to detect the chromium ion in aqueous solutions [15–20]. Several ligands can coordinate chromium ions on metal NPs. Tween 20 [15], glutathione [16], 11-mercaptoundecanoic acid [17], and 5,5′-dithio-*bis*-(2-nitrobenzoic acid) [18,19], and citric acid [20] were used to modify Au nanostructures. A series of heterotripodal receptors for the Cr(III) binding sites were synthesized using copper NPs [21].

Amino acids are used as a biocompatible approach to functionalize AuNPs [22,23]. L-Lysine was used to detect the Hg(II) and Cu(II) ions in aqueous solutions [24]. Despite the binding of L-methionine (Met) of copper, silver, zinc, and etc [25,26] in aqueous solutions, it is not certain yet how the metal complexes interact with metal nanoparticles. Considering that a required amount of Cr(III) is necessary in carbohydrate mechanism [8,9], an introduction of the amino acid to functionalize AuNPs would be beneficial for the detection of Cr(III) in biological media. Several studies have reported on chromium methionine complexes [27–29], but no published works have appeared regarding chromium detection using AuNPs. In the present work, we introduce Met–Cr(III) complex, which is bound to AuNPs, as a method for confirming dissimilar adsorption behavior of Cr(III) that yields a difference in spectral intensity. We report a Cr(III) detection method using AuNPs by means of combined methods of colorimetric, UV–vis, and SERS. Met after the complex with the ion is sensitive and selective for Cr(III) in aqueous AuNP solutions. On the basis of absorbance measurements of the aggregated AuNPs at 650 nm, a sensitive detection of Cr(III) as low as 300 nM was achieved compared with the previous reports [15–20].

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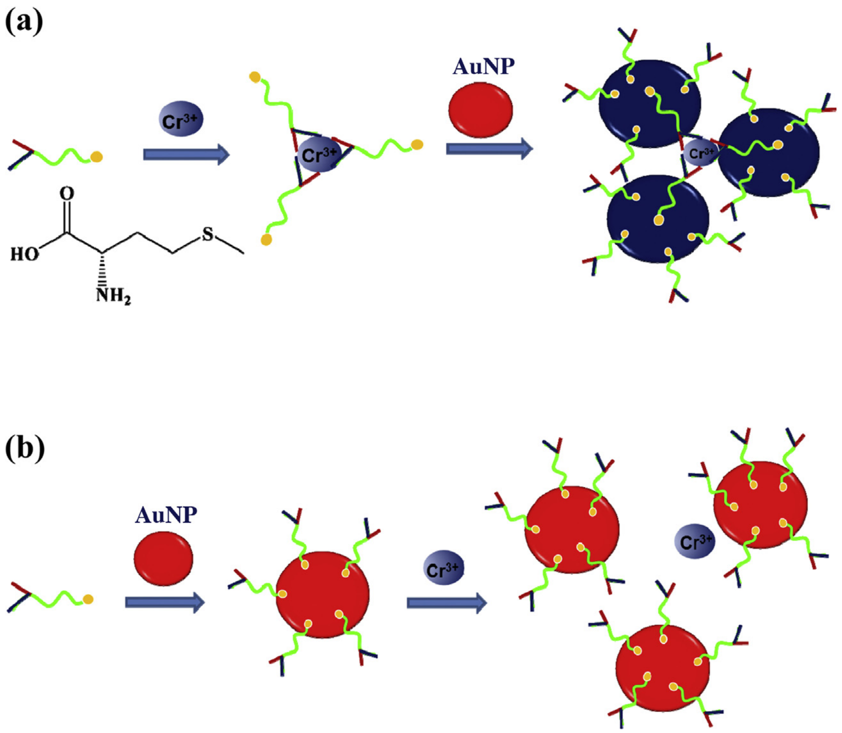

Fig. 1. Schematic diagram of the detection of Cr(III) with AuNPs. (a) Met was bound to Cr(III). The Met–Cr(III) complex was treated with AuNPs. We have marked the sulfur atom and the carboxylic and amino groups in a different way for better presentation. The yellow dot represents the sulfur atom, whereas the carboxyl and amino groups are depicted using y-shaped pincers colored red and blue, respectively. (b) Control experiment: Met was assembled on AuNPs. The subsequent Cr(III) did not cause aggregation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Experimental

2.1. Chemicals and sample preparations

Cr(III) and the other ionic substances of NaCl, KNO_3, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $Cr(NO_3)_3$, $Mn(NO_3)_2$, $Fe(C_2O_4)$, $Fe(NO_3)_3$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, NH_4NO_3, $Cd(NO_3)_2$, $Hg(NO_3)_2$, $Pb(NO_3)_2$, and $K_2Cr_2O_7$ (or Na_2CrO_4) along with hydrogen tetrachloroaurate trihydrate, Met, and *p*-aminobenzenethiol (*p*-ABT) were purchased from Sigma Aldrich (St. Louis, USA). We prepared AuNPs by slightly modifying the protocol in a previous report [30]. Briefly, the vial was cleaned with piranha solution and allowed to rest for 30 min to 1 h. Then, the vial was washed three times with acetone, ethanol, and triply distilled water. We also maintained the solution level for 1 h by adding triply distilled water. We tested triply distilled water, tap water, river water, and seawater to check the applicability of our methods. The river water samples were collected from the Han River (Seoul, Korea) and the seawater samples were taken from the Yellow Sea (Tae-an, Chungcheongnam-do Province, Korea).

2.2. Equipment and characterization methods

The morphologies of AuNPs were checked using a JEOL JEM-3010 transmission electron microscope. The diameters of pristine AuNPs were ~20 nm from the TEM measurements. UV–vis absorption spectra were obtained using a Mecasys spectrophotometer. To further check the adsorption behavior, SERS measurements were performed on AuNP surfaces [31]. Raman spectra were obtained using a Renishaw Raman confocal system model RM 1000 spectrometer equipped with an integral microscope (Leica DM LM) at the irradiation of 632.8 nm radiation from an air-cooled He–Ne laser (Melles Griot Model 25 LHP 928). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used to estimate the atomic compositions of the prepared samples with an ICAP-7400 analyzer from Thermo Scientific (Waltham, USA) with a detection limit better than 10 ppb for the tested metal species. For the Hg measurements, a CETAC M-7500 mercury analyzer from Parma Company (Omaha, USA) was used with a detection limit of 0.6 ppb. In order to identify the Cr species, we performed X-ray photoelectron (XPS) spectra using a Sigma Probe instrument from Thermo VG using an Al-Kα monochromatic source. We obtained Fourier transform infrared spectroscopy (FT-IR) data to examine the structural change of Met after the binding Cr(III) using a MIRacle ZnSe attenuated-total reflection accessory from Pike Technologies (Madison, USA) and a FT-IR 6700 spectrometer equipped with a narrow band HgCdTe detector from Thermo Nicolet (Waltham, USA).

2.3. Sample preparation

For the UV–vis experiment, in the first step, Met (0.12 M, 3.3 μL), Cr(III) (1 mM, 1 μL), and ultrapure water (95.7 μL) were all placed in a 1.5 mL Eppendorf tube, and then stirred and stabilized over 60 min at room temperature. In the second step, 100 μL of AuNPs was added to form the Met–Cr(III)–AuNP complex. In the third step, 800 μL of ultrapure water was added to the mixture. The pH was maintained at 5.35 for the formation of stable Met–Cr(III)–AuNP assemblies. For the SERS experiment, 91.7 μL of H_2O, 5 μL of Cr(III) (1 mM), and 3.3 μL of Met (0.12 M) were mixed and stirred for over 60 min at room temperature. Subsequently, 100 μL of AuNPs and 1 μL of *p*-ABT (10 mM) were added to the mixture, and the SERS spectra were observed. The excessive amount of Met was used to interact AuNPs in an effective way and monitor the resulting spectral change.

For the XPS experiments, 10 μL of Cr(III) (1 mM, in distilled water) and 33 μL Met (0.12 M) were mixed and stirred for over