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A simple and rapid method for direct determination of Al(III) based on the enhanced resonance Rayleigh scattering of hemin-functionalized graphene-Al(III) system

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ABSTRACT

A novel method for direct determination of Al(III) by using hemin-functionalized graphene (H-GO) has been established based on the enhancement of resonance Rayleigh scattering (RRS) intensity. The characteristics of RRS spectra, the optimum reaction conditions, and the reaction mechanism have been investigated. In this experiment, the Al(III) would exist in sol–gel $Al(OH)_3$ species under the condition of pH 5.9 in aqueous solutions. When H-GO existed in the solution, the sol–gel $Al(OH)_3$ would react with H-GO and result in enhancement of RRS intensity, owing to the enhanced hydrophobicity of H-GO surface. Therefore, a simple and rapid sensor for Al(III) was developed. The increased intensity of RRS is directly proportional to the concentration of Al(III) in the range of 10 nM–6 μM, along with a detection limit of 0.87 nM. Moreover, the sensor has been applied to determination of Al(III) concentration in real water and aspirin tablet samples with satisfactory results. Therefore, the proposed method is promising as an effective means for selective and sensitive determination of Al(III).

1. Introduction

Graphene, a two-dimensional honeycomb structure and single-atom-thick carbon material, has become one of the research focuses recently. Due to its excellent physical and chemical properties, such as large surface [1], high strength [2], excellent electric [3] and thermal conductivity [4], graphene has been widely used in many fields including batteries [5], sensors [6,7], and drug carriers [8], etc. Though a lot of studies on graphene material have been published in the past years [9–12], some properties of graphene material are still challenging for researchers from various fields, such as chemical inertness and instability in aqueous solutions, which limits graphene applications. Therefore, it is extremely essential to functionalize graphene. According to the different connecting ways between the modifying group and graphene, the usual ways to functionalize graphene include covalent [13–15] and non-covalent [16–18] methods. The covalently functionalized graphene possesses the characteristic of improved solubility and dispersion, and could also be used to prepare a variety of functional materials by derivatization reaction between connected groups. For example, Veca et al. obtained the poly (vinyl alcohol)-functionalized graphene via the esterification reaction between the carboxyl group on the surface of graphene and the hydroxyl groups of poly (vinyl alcohol) [19]. However, the π–π structure of functionalized graphene, obtained from covalent modification, is very easy to be destroyed during the reaction. The non-covalently functionalized graphene is obtained by electrostatic forces, the π–π bond, the van der Waals force, hydrophobic and hydrophilic interaction between the surface of graphene and the molecules, without undermining the original structure of graphene. Because this connection will not damage the π–π structure of graphene, the non-covalent connection method is more favored by researchers when functionalizing graphene [17,20,21]. In this work, hemin-functionalized graphene (H-GO) has been successfully obtained by π–π stacking interaction between graphene oxide and hemin in the presence of hydrazine and ammonia solution [22].

On the other hand, it is well known that aluminum is the third most prevalent element and the most abundant metal in the earth's crust. In recent five decades, aluminum has been widely applied in manufacturing industry, electrical industry, cooking utensils, packaging, painting, deoxidizing agent, construction industry, and clinical drugs, etc. [23,24]. However, Al(III) could be fatal to the growth and function of plant roots in acid soils [25]. Al(III) would also be slowly and imperceptibly accumulated in the human body and lead to various diseases, such as osteomalacia [26], breast cancer [27], Parkinson's disease [28], and dialysis encephalopathy [29]. According to the World Health Organization report, the average daily intake of aluminum for everyone is approx 3–10 mg day^{-1} and tolerable weekly aluminum intake in the human body is estimated to be 7 mg kg^{-1} body weight [30–32]. Therefore, it is very necessary to detect Al(III). Currently, atomic absorption spectroscopy [33], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [34], voltammeters [35], membrane bioreactor [36], high performance liquid chromatography [37], and fluorescence spectrum

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methods [38] are mainly utilized for Al(III) detection. However, these methods display various shortcomings to some extent, such as manipulating complex, requiring expensive equipment, poor selectivity, and low sensitivity. So, it is very important to develop a method for detecting Al(III) with high selectivity and sensitivity. Resonance Rayleigh scattering (RRS) technique has the advantages of rapidity, simple operation, and high sensitivity. In recent years, the technique has been applied to detect biological macromolecules, metal ions, and nonmetal ions, etc. [39–42]. Moreover, several reports have focused on RRS approach to Al(III) monitoring based on ethyl violet-DNA complex [43], morin–surfactant complex [40], and aggregation of protein [44].

In this paper, H-GO was used as a sensor for detecting Al(III) based on resonance Rayleigh scattering. We discovered that the presence of Al(III) will enhance the RRS intensity of H-GO, which could be due to the induction of sol–gel $Al(OH)_3$. And the results showed that the increased RRS intensity has a better linear relation with the concentration of Al(III) in a certain range. Moreover, this method has good selectivity and high sensitivity, and the detection limit can be down to 0.87 nM. What is more, the method has been successfully applied to the determination of Al(III) concentration in real water and aspirin tablet samples. Thus, a rapid and simple RRS method for the determination of Al(III) was developed.

2. Experimental section

2.1. Synthesis of hemin-functionalized graphene

Graphene oxide (GO) was synthesized from graphite powder according to Hummer's method with little modification [45]. Hemin-functionalized graphene was synthesized according to the literature [23]. In a 10 mL vial, 2.5 mL of 0.5 mg mL^{-1} graphene oxide solution was mixed with 1.3 mg of hemin and 2.5 μL of ammonia solution (25–28 wt.% in H_2O), immediately following 3.7 μL of hydrazine solution (80 wt.% in H_2O). After being shaken for 5 min on a whirlpool oscillator, the vial was put in a water bath (65 °C) for 3.5 h. The obtained black solution was centrifuged at 1300 rpm for 30 min to remove the hemin without reaction.

2.2. Detection of Al(III)

The general detection procedures were as follows: solutions of acetate buffer (492 μL, 0.1 M, pH 5.9), H-GO (3 μL, 1 mg mL^{-1}), and 5 μL of aluminum ion solutions with various concentrations were added in turn to a centrifuge tube (1.5 mL), and the mixtures were incubated for 2 min at room temperature. The resonance Rayleigh scattering spectra were recorded with synchronous scanning at $\lambda_{em} = \lambda_{ex}$ in the wavelength range of 220–600 nm. The enhanced RRS intensity (I), with the detection wavelength of 415 nm, was obtained as $\Delta I = I - I_0$, where I and I_0 were the RRS intensity of the system with and without Al(III), respectively.

2.3. Procedure for detection of Al(III) in aspirin tablet sample

The pretreatment of aspirin tablets is based on the method of detecting Al(III) in Weishuping tablets [46]. Firstly, 10 aspirin tablets were ground into a powder, then, 0.5927 g of the powder (equivalent to 8 aspirin tablets) was accurately weighed in a 50 mL beaker and 20 mL of 6 M hydrochloric acid solution was added. Subsequently, the above solution is heated in boiling, and then cooled to room temperature. The mixture was filtered and the filtrate was diluted to 1000 mL with ultrapure water. Finally, 5 μL of diluted solution and 3 μL of 1 mg mL^{-1} H-GO were added to 492 μL of acetate buffer (pH 5.9). The mixture was well vortexed and incubated for 2 min, and the RRS intensity was then measured on the Hitachi F-2700 fluorescence spectrophotometer. Chemicals, apparatus, and more detailed experimental protocols are given in the Supplementary Information.

3. Results and discussion

3.1. Resonance Rayleigh scattering spectra

The RRS spectra of reduced graphene oxide-Al(III) (R-GO-Al(III)), graphene oxide-Al(III) (GO-Al(III)), and the hemin-functionalized graphene-Al(III) (H-GO-Al(III)) system were recorded using synchronous scanning from 220 to 600 nm with $\lambda_{ex} = \lambda_{em}$. The results are shown in Fig. 1. Under the experimental conditions, the RRS intensities of H-GO (curve 7) and Al(III) (curve 5) were very weak. However, the spectrum of H-GO-Al(III) showed that the RRS intensity of the system was markedly enhanced and the maximum scattering peak was located at 415 nm (curve 1). In addition, the RRS intensity of GO (curve 6) was lower than that of the same concentration R-GO (curve 3), which showed the dispersion of graphene oxide is better than that of graphene. On the other hand, the RRS intensities of R-GO-Al(III) (curve 2) and GO-Al(III) (curve 4) systems, compared respectively to that of the R-GO (curve 3) and GO (curve 6), had not been significantly enhanced. Therefore, Al(III) could not markedly enhance the RRS intensity of R-GO or GO, and the presence of hemin is very important for the detection of Al(III) in this experiment.

3.2. Optimization of experimental parameters

The experiment investigated the effect of solution acidity and the results showed that variation of pH value would greatly influence the RRS intensity of the H-GO-Al(III) system. As shown in Fig. 2, the RRS intensity of H-GO enhanced when pH was less than 5.9, which could be because the protonation of oxygen-containing functional groups on the H-GO surface caused the aggregation of H-GO at low pH. In addition, when the pH was greater than 5.9, the aluminum had a stronger signal of RRS. And when the pH value was 5.9, the RRS intensities of H-GO and aluminum were relatively lower and stable, and the value of $\Delta I/I_0$ reached the maximum value. Therefore, pH 5.9 is selected as the optimum acidity for detection Al(III).

As previous literature reported [47], under different pH, the existence forms of Al(III) are various. When Al(III) concentration is relatively low and pH values is between 5.5 and 7.5, the dominate Al(III) species are $Al(OH)_3$, which are in the form of sol–gel rather than precipitation in fresh solution. And the above view was verified by adding a certain amount of EDTA to the reaction solution in this work. If the existence forms of Al(III) were dissolved Al^{3+}, the RRS intensity of system would decrease when the EDTA was added to the solution. However, the results shown in Fig. 3 indicated that the enhanced RRS intensity

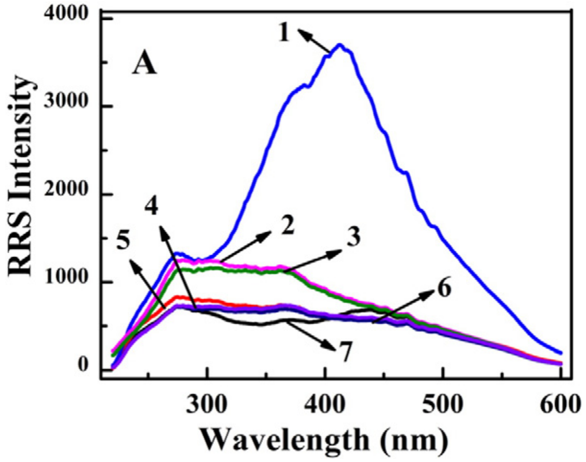

Fig. 1. Resonance Rayleigh scattering spectra of the H-GO-Al(III) system: 1. H-GO + Al(III); 2. R-GO + Al(III); 3. R-GO; 4. GO + Al(III); 5. GO; 6. Al(III); 7. H-GO. Concentrations of H-GO, Al(III), R-GO, and GO are 6 μg mL^{-1}, 6 μM, 3 μg mL^{-1}, and 3 μg mL^{-1}, respectively. Acetate buffer solution (20 mM, pH 5.9).