



Modified graphene oxide sensors for ultra-sensitive detection of nitrate ions in water

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ABSTRACT

Nitrate ions is a very common contaminant in drinking water and has a significant impact on the environment, necessitating routine monitoring. Due to its chemical and physical properties, it is hard to directly detect nitrate ions with high sensitivity in a simple and inexpensive manner. Herein with amino group modified graphene oxide (GO) as a sensing element, we show a direct and ultra-sensitive method to detect nitrate ions, at a lowest detected concentration of 5 nM in river water samples, much lower than the reported methods based on absorption spectroscopy. Furthermore, unlike the reported strategies based on absorption spectroscopy wherein the nitrate concentration is determined by monitoring an increase in aggregation of gold nanoparticles (GNPs), our method evaluates the concentration of nitrate ions based on reduction in aggregation of GNPs for monitoring in real samples. To improve sensitivity, several optimizations were performed, including the assessment of the amount of modified GO required, concentration of GNPs and incubation time. The detection methodology was characterized by zeta potential, TEM and SEM. Our results indicate that an enrichment of modified GO with nitrate ions contributed to excellent sensitivity and the entire detection procedure could be completed within 75 min with only 20 μ l of sample. This simple and rapid methodology was applied to monitor nitrate ions in real samples with excellent sensitivity and minimum pretreatment. The proposed approach paves the way for a novel means to detect anions in real samples and highlights the potential of GO based detection strategy for water quality monitoring.

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1. Introduction

Nitrate ions are widely found in the environment due to its high solubility. It is known that contamination of water by nitrate ions due to agricultural and industrial waste can pose a threat to environmental water quality [1,2]. High concentration of nitrate ions in drinking water may cause serious illnesses such as birth defects, spontaneous abortions, intrauterine growth restriction and potential cancer risk [3–6]. A recent investigation for the presence of nitrate ions by the Environmental Protection Agency (EPA) indicated that the maximum contamination level (MCL) was exceeded in the self-supplied water consumed by more than 4 million Americans, necessitating advanced and sensitive methods to detect ions in water [4,7]. Further, long-term accumulation of nitrate ions in the environment may be a potential risk to animals. Thus, there is growing demand for the development of simple and cost-effective methods for routine monitoring of

nitrate ions with high sensitivity for both human and animal health and environment. Until now, various analytical techniques, such as chromatography, electrochemical method, Raman spectroscopy and fluorescent spectroscopy, have been used for nitrate ion detection, but these methods require complex and expensive instrumentation [8–15]. Besides, colorimetric and absorption spectrum-based methods that utilize gold nanoparticles (GNPs) have also been reported [4,16], to provide a more convenient and economical route for routine monitoring of nitrate ions. In the past methods, nitrate ions or its reduced product, nitrite ions, cross-links the modified GNPs to generate a signal and the concentration of nitrate ions was determined by monitoring the increase in aggregation of GNPs. However, this approach is not sensitive because at lower concentrations, nitrate ions cannot trigger an observable aggregation of GNPs, and hence not detectable [17]. Meanwhile, it is known that some of the common anions in real water samples such as Cl^- , S^{2-} and SO_4^{2-} can also induce the aggregation of GNPs, and thus can contribute to non-specific signals and distort the detection of nitrate ions in real sample such as surface water or ground water. Therefore the reported methods based on

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absorption spectroscopy usually require complex pretreatment of real samples to minimize the influence from other materials when testing real samples. Furthermore, although some commercial instruments for nitrate ions detection are available, their sensitivity is in the range between 322 and 1046.5 μM (20–65 ppm). Hence, a rapid and facile method for the detection of nitrate ions at low concentration in real samples is still a challenge.

Graphene and graphene oxide (GO) have drawn enormous attention due to their excellent physical and chemical properties since its discovery in 2004 [18]. The electronic and chemical properties of graphene and GO have been investigated by various groups. A notable characteristic of graphene and GO is their interaction with other molecules. It has been demonstrated that graphene and GO can be used to load and deliver drugs such as nanocarriers [19,20], because of the capability of graphene or GO to enrich drug molecules. When this enrichment is utilized in an analytical application, the sensitivity of detection (ie., the limit of detection, LOD) using graphene or GO can be greatly improved, because the enrichment procedure can increase the analyte concentration on the graphene or GO substrate in solution [21,22]. For instance, Wen et al. has reported an ultra-sensitive surface enhanced Raman scattering approach to monitor folic acid based on GO/Ag nanoparticles hybrids. Here they show a dramatic improvement in sensitivity due to the enrichment capability of GO sheet to folic acid in solution; meanwhile the enrichment of GO also improved the detection of folic acid in serum, suggesting that an interaction between GO and target molecules could improve the detection sensitivity of nitrate ions in real samples [23]. Recent report on the absorption of nitrate ions by graphene sheet in water further highlights the enrichment potential of graphene sheet to nitrate ions [24], further implying the possibility of enhancement sensitivity of nitrate detection utilizing GO. Besides, the large surface and its low manufacturing cost can make GO an excellent choice for analytical applications. Further, compared with graphene, GO could be a better choice for the development sensors due to its high solubility and stability in water.

In this effort we report on an ultra-sensitive nitrate ion detection method based on the absorption spectrum utilizing GO and GNPs as substrates. Our approach can directly detect nitrate without the reduction step, thereby making the detection procedure simple and direct while avoiding the use of toxic chemicals. Different from the previous works based on GNPs [4,16], in our scheme, GNPs interacts with amino group modified GO instead of directly interacting with nitrate ions because very low concentration of nitrate ions cannot trigger the aggregation of GNPs which has been a key limitation to detecting at low levels in prior works [17]. In our detection procedure, amino group modified GO can cause aggregation of GNPs, while the interaction between nitrate ions and modified GO will reduce this aggregation. Hence, based on the reduction of GNPs aggregation measured by the absorption spectrum, the concentration of nitrate ions can be determined. Because the most common anions also induce aggregation of GNPs and can influence the detection by contributing to non-specific aggregation, the previous detection approaches for nitrate detection based on the increased aggregation levels of GNPs was not sensitive and furthermore, these methods required complex pretreatment. Compared with the previous approaches, our method based on monitoring the reduction in GNP aggregation showed better potential to detect nitrate ions in real samples. Based on the demonstrated adsorption potential of GO sheet to nitrate ions and the interaction between amino groups and nitrate ions [16,24], the enrichment of nitrate ions in the sample with amino group modified GO sheets contributed to a highly sensitive nitrate ion detection protocol as demonstrated from our experiments. With serial optimizations of detection conditions the lowest detected concentration of nitrate ion is 5 nM in deionized

water, which is much lower than the methods based on absorption spectroscopy reported by previous work (the limit was 161 μM) [4]. Using water samples obtained from the local river and purposefully contaminating it with a known concentration of nitrate ions a similar sensitivity was demonstrated with minimum pretreatment. The developed method thus shows strong potential for nitrate ion monitoring in the environment in a simple and cost-effective manner. We believe that the developed analytical strategy based on monitoring the reduction in aggregation of GNPs can be used to detect other ions with high specificity and sensitivity.

2. Material and methods

2.1. Chemicals and reagents

Sodium nitrate (NaNO_3) was purchased from JT Baker Chemical Co. Sodium acetate (NaAc), sodium carbonate (Na_2CO_3) and sodium chloride (NaCl) were obtained from Mallinckrodt Chemicals, HAuCl_4 , sodium citrate, ethylenediamine ($\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$), sodium bromide (NaBr), sodium iodide (NaI), sodium sulfide (Na_2S) and sodium sulfate (Na_2SO_4) were from Sigma Chemical Co. GO was purchased from Cheap Tubes Inc. All reagents are used as received without further purification.

2.2. Gold nanoparticles preparation

Glasswares used in the following procedures were cleaned in a bath of freshly prepared 3:1 $\text{HCl}:\text{HNO}_3$ (aqua regia) and rinsed thoroughly in milli-Q grade water prior to use. Colloidal GNPs were prepared according to the reported method [25]. Briefly, 1 ml of 1% HAuCl_4 was added to 100 ml H_2O . The obtained solution was heated to boiling under stirring, followed by injection of 2 ml of 1% sodium citrate solution. After continued boiling for 10 min, the solution was cooled to room temperature to obtain a wine red color. For detection, 4 ml of GNPs was centrifuged at 8000 rpm for 10 min and washed with H_2O , and then redispersed in 0.2 ml H_2O . The concentration of GNPs was determined by the reported method [26].

2.3. Graphene oxide modification

GO modification with amino groups was carried out based on the method reported by Lee [27]. Generally, GO is dissolved in ethanol at a concentration of 1 mg/ml. 12 μl of ethylenediamine is added to 0.3 ml of 1 mg/ml GO ethanol solution and the obtained mixture was stirred slowly at room temperature overnight. The product was then washed with ethanol and water 3 times respectively, and redispersed in water at a concentration of 0.5 mg/ml.

2.4. Detection of nitrate

During a typical detection procedure, 20 μl of 0.5 mg/ml amino group modified GO solution was mixed with 20 μl of nitrate ions in deionized water and the mixture was incubated for 1 h at room temperature. Then 5 μl of this mixture was added to 5 μl of concentrated GNPs. After 5 min, 266 μl of H_2O was added and the UV-vis spectra was recorded.

To prepare real samples, river water (pH was 7.0) was obtained from a local river and centrifuged at 10,000 rpm for 10 min to remove large precipitates such as floating sediments. The samples were then purposefully contaminated with nitrate ions to serial concentrations. To detect nitrate ions, 20 μl of 1.0 mg/ml amino group modified GO solution was mixed with 20 μl of the sample solution. After 1 h of interaction of modified GO with nitrate ions

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