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Highly sensitive electrochemical determination of sulfate in $PM_{2.5}$ based on the formation of heteropoly blue at poly-L-lysine-functionalized graphene modified glassy carbon electrode in the presence of cetyltrimethylammonium bromide

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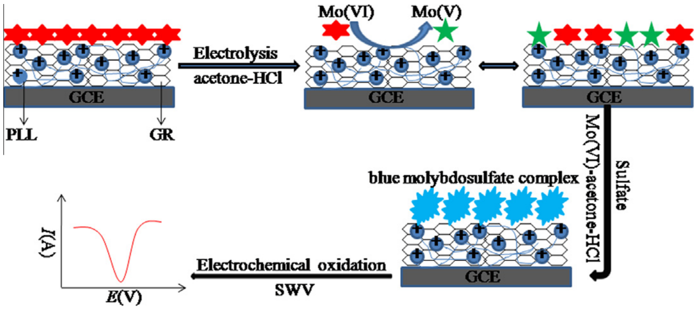
HIGHLIGHTS

- Voltammetric detection of sulfate based on the oxidation current of heteropoly blue.
- Poly-L-lysine-functionalized graphene was used as a matrix.
- Cetyltrimethylammonium bromide was employed to enhance the sensor sensitivity.
- Sulfate in $PM_{2.5}$ was successfully assayed by the proposed approach.
- The developed method had a high sensitivity and a wide linear range.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple and sensitive electrochemical sensor based on the formation of heteropoly blue at poly-L-lysine (PLL)-functionalized graphene (GR) modified glassy carbon electrode (GR-PLL/GCE) was developed to detect sulfate in the presence of cetyltrimethylammonium bromide (CTAB). This method was based on the oxidation currents of the blue complex formed via 40 s electrolysis of Mo (VI)–acetone–HCl solution containing sulfate at 0.1 V vs. SCE and sulfate concentration. The structure and morphology of GR, PLL and GR-PLL were examined by Raman, Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The fabricated sensor was further characterized using cyclic voltammetry (CV). Under optimum conditions, the sensor displayed a wide linear range of 0.8–1000 μM for sulfate concentration with the coefficient of determination of 0.9996 and a detection limit of 0.26 μM. The proposed sensor was further employed to detect sulfate in fine particles ($PM_{2.5}$, particulates with aerodynamic diameters <2.5 μm). The results obtained were in good agreement with those of using ion chromatography (IC), which indicates that this novel voltammetric sensor has promising applications for the detection of sulfate in environmental fields.

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1. Introduction

Graphene, with a unique planar single layer of sp^2 bonded carbon atoms well ordered in a hexagonal configuration, is the youngest member of the carbon family [1–4]. It has shown many interesting and exciting properties, including large specific surface area, exceptional electrical and thermal conductivity, excellent electrochemical stability, outstanding mechanical flexibility, unusual quantum Hall effect, high optical transparency, and manifestation of catalytic properties toward all kinds of electrochemical analytes [5–8]. Since first reported in 2004, it has attracted tremendous research interest and been applied in various fields such as nanoelectronics, nanocomposites, supercapacitors, fuel cells, batteries, and sensors [9–11]. Graphene also exhibits many advantages over the other two important carbon materials namely graphite or carbon nanotubes (CNTs). Addition to its much greater surface area, graphene is more accessible and cheaper than CNTs and does not contain metallic impurities with toxicological hazard as CNTs do, and the graphene-based electrodes have lower over-potentials than those of graphite-based owing to their greater and more uniform distribution of the electroactive sites [12,13]. Moreover, new types of graphene-based materials with desirable properties can be produced by modifying its structure as reported in the literature [14,15]. These attributes mentioned above make graphene an ideal material for electrochemical sensing applications [12,16,17].

However, graphene sheets can aggregate easily and irreversibly through the strong van der Waals interactions when they were dispersed in solution and this poor dispersion has limited their applications [18–20]. Various strategies have been explored to obtain dispersed graphene sheets [12]. Polymer materials, especially conducting polymers, have been employed for graphene modification owning to their excellent optical and electrical qualities [21]. Among these, poly-L-lysine (PLL) has received particular attention owing to its plentiful active amino groups, good biocompatibility, relatively good solubility in water, and a flexible molecular backbone [22]. Also, it can promote electron transfer and significantly reduce over-potentials [23]. Besides, PLL (pKa = 10.4) can be used for the accumulation of anion because a large number of positively charged active amino groups are available in its structural framework [24,25]. Some works have reported the better performance of graphene nanosheets functionalized by PLL. For instance, Niu et al. have proposed a covalent modification strategy to prepare water-soluble graphene functionalized by PLL, which shows great application in biosensors [26]. Here, an electrochemical sensor based on the PLL functionalized graphene was proposed.

In the recent years, fine particles ($PM_{2.5}$, particles less than 2.5 μm in diameter) have attracted significant attention from the public and the government owing to its adverse effects on human health, air quality, visibility and climate change [27–29]. There is an urgent need for governmental regulatory bodies to carry out monitoring and analysis components in $PM_{2.5}$ worldwide. Sulfate, usually produced by homogeneous or heterogeneous oxidation of SO_2, is a primary component of $PM_{2.5}$ mass [30–32]. It plays a significant role in many ways including respiratory diseases [33], light extinction effect [34], hydrosphere and acidity of aerosols [35,36]. Thus, to develop a rapid and sensitive method for the detection of sulfate in $PM_{2.5}$ is of great importance. Existing methods for detecting sulfate in $PM_{2.5}$ are Dionex gas particle ion chromatography (GP-IC), aerodyne aerosol mass spectrometer (AMS), particle-into-liquid sampler with ion chromatograph (PILS-IC), gas and aerosol monitoring system (GAMS), and so on [37,38]. But they have several drawbacks such as complexity, large-scale, high-cost, and unfavorable portability. Compared with these methods, the electrochemical techniques can be used as attractive alternatives for easier and cheaper detection of sulfate owing to their rapid response, high sensitivity, good reliability, favorable portability, low power consumption, simple operation and suitability for automation [39,40]. Various electrochemical methods for sulfate determination, mainly potentiometric methodologies, have been developed. It is notable that the most prominent feature for these techniques is the use of ion-selective electrodes (ISEs) [41–43]. But the obtained sulfate ISEs are insufficiently sensitive and selective for the analysis of real samples [44]. The direct voltammetric determination of sulfate is very difficult because of its high over-potential and voltammetry based works seldom have been reported. Nevertheless, T. Osakai et al. have developed an indirect voltammetric technique for sulfate determination based on the fact that the oxidation current of the heteropoly blue produced at the electrode surface by one minute electrolysis of Mo (VI)–acetone–HCl solution containing sulfate was proportional to the sulfate concentration [45]. It was carried out by cyclic voltammetry on the bare GCE, but it is not feasible to detect sulfate in $PM_{2.5}$ for its poor sensitivity. Therefore, more effort should be focused on utilizing new electrochemical techniques and advanced materials to modify the electrodes for the purpose of achieving sensitive and reliable detection of sulfate.

Surfactants, a type of amphiphilic molecules with the hydrophilic group at one end and the hydrophobic group at the other, have been widely used in electrochemistry and electroanalytical chemistry because of the enhancement effect and the ability to improve the performance of the electrode/solution interface [46,47]. They can be adsorbed onto the electrode surface to form surfactant films, which may change the over-potential of the electrode and affect the rate of electron transfer [48]. Based on their special properties, a few surfactants, including the long-chain cationic surfactant-cetyltrimethylammonium bromide (CTAB), have been exploited to fabricate new electrochemical sensors [49–51]. As far as CTAB is concerned, a surfactant bilayer will primarily be formed on the electrode surface when its concentration is higher than the critical micelle concentration (CMC). This bilayer formation will lead to the reversion of the charge on the external electrode, providing a lot of sorption sites for anions [52]. In the present work, the positively charged exchange sites provided by CTAB can promote the sorption of the involved anions (such as sulfate and molybdate) onto the electrode surface, which contributes to the formation of the anion complex-heteropoly blue. As a result, the oxidation signals will be enhanced.

Herein, based on the electrooxidation of heteropoly blue electrodeposited on the PLL-functionalized graphene modified glassy carbon electrode and the CTAB sensitization, a square-wave voltammetric method for sulfate determination was developed. It showed good performance with wide linear range and excellent stability. To the best of our knowledge, no work has reported on the voltammetric detection of sulfate using PLL-functionalized graphene relevant electrochemical sensors in the presence of CTAB. And for the first time, the proposed electrochemical method was used to detect sulfate in water extracts of $PM_{2.5}$ samples, and the results obtained were consistent well with those obtained by ion chromatography.

2. Experiments

2.1. Reagents and materials

Sodium molybdate dehydrate (>99%), cetyltrimethylammonium bromide (CTAB, >99%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), graphene (GR) was produced by Nanjing Ji Cang Nano Technology Co., Ltd. (Nanjing,