



Controlled synthesis of reduced graphene oxide supported silver nanoparticles for selective and sensitive electrochemical detection of 4-nitrophenol



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ABSTRACT

An electrochemical sensing platform made of a reduced graphene oxide-silver (rGO-Ag) nanocomposite was developed for the detection of 4-nitrophenol. The synthesis of the nanocomposite was monitored at different reaction times (2 h, 6 h, 10 h and 15 h) in modified Tollens' test and characterized using UV-visible absorption spectrum, transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectroscopy analyses. Completely spherical Ag nanoparticles (NPs) were found at a reaction time of 15 h with an average particle size of 16 nm. The nanocomposites prepared with different reaction times were used for the electrocatalytic reduction of 4-NP, and the rGO-Ag (15 h) nanocomposite-modified glassy carbon (GC) electrode displayed a higher faradaic current at an overpotential of -0.5 V toward 4-NP reduction. The rGO-Ag (15 h) nanocomposite-modified electrode was used for the square wave voltammetric (SWV) detection of 4-NP in a 0.1 M phosphate buffer (pH 7.2), and it showed a good sensitivity toward 4-NP detection even for a nanomolar concentration. The nanocomposite exhibited multi-linear ranges and 4-NP detection limit was found to be 1.2 nM. The present sensor was stable and selective to 4-NP in the presence of its structural analogues such as 2-nitrophenol (2-NP), 2-aminophenol (2-AP), 3-aminophenol (3-AP), 4-aminophenol (4-AP), and 2,4-dichlorophenol (2,4-DCP). The rGO-Ag nanocomposite could be successfully applied for the determination of 4-NP in real water samples, and good recoveries were found.

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1. Introduction

Phenolic compounds are frequently utilized in many industrial processes and partially released into soil and water environments [1]. Among these, nitrophenols are widely involved in the production of pesticides, dyes, and pharmaceuticals. They are anthropogenic, toxic, inhibitory, and bio-refractory organic compounds [2]. 4-Nitrophenol (4-NP) is one of the most abundant nitrophenols, and is a hazardous substance that causes substantial damage to the environment as well as in living systems, because of its toxicity and high stability [3]. Its strong chemical stability and immunity to microbial degradation makes the detoxification of 4-NP-contaminated water a very difficult process [4]. Further, the acute ingestion or inhalation of 4-NP by humans can cause headaches, drowsiness, nausea, and cyanosis. Because of its high

toxicity, 4-NP was cited in the List of Pollutants of the US Environmental Protection Agency, which set the permitted limit of 4-NP in drinking water at $0.43\ \mu\text{M}$ [5]. Thus, the determination of 4-NP has become vital for the protection of the environment.

Numerous techniques have been adopted for the determination of 4-NP, including real sample analyses such as capillary electrophoresis [6], spectrophotometry [7], high performance liquid chromatography [8], flow-injection analysis [9], and enzyme-linked immunosorbent assay [10]. However, some of these techniques are comparatively expensive, time consuming, and involve difficult instrument requirements for environmental testing. Thus, the development of a less time consuming and more cost effective technique is essential for the determination of 4-NP in real water samples. Electrochemical methods have shown great potential for 4-NP determination because of the advantages of low-cost instruments, easy operation, good sensitivity, short run times with simple sample pre-treatment, and *in situ* detection [11,12]. However, the electrochemical detection of 4-NP at bare electrodes offers less sensitivity and suffers from high overpotential, and interference issues [13]. Therefore, chemically modified electrodes

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are widely employed to avoid these problems, leading to the proposal of highly efficient electrochemical sensors for the determination of 4-NP [14–16].

Fabricating a competent electrochemical sensor for the sensitive detection of 4-NP has generated much interest among researchers. Although many modified electrodes based on carbon nanotubes [17,18], metal nanoparticles (NPs) [19,20], and ionic liquids [21] have previously been reported for the determination of 4-NP with satisfactory results, designing a new electrochemical sensor based on novel materials with excellent electrocatalytic properties using a simpler preparation remains a challenge. Silver nanoparticles (Ag NPs) based electrochemical sensors are highly preferred for the determination of 4-NP because of their low cost and the conductivity of Ag is higher than other noble metals such as Au, Ag, Pd and Pt [22]. Ag NPs acted as nanoelectrocatalyst and could facilitate more efficient electron-transfer process during electrocatalysis [23]. Particularly, Ag NPs are a well-known electrocatalyst for the reduction of nitro-aromatic compounds [15,23]. Previously, a modified Tollen's test was used for the synthesis of a variety of Ag nanostructures with interesting morphologies by several research groups [24–26]. The modification of Tollen's test with surfactants, polymers, or support materials is important for the controlled synthesis of Ag NPs. Further, there have been a limited number of reports on the synthesis of Ag NPs supported on a reduced graphene oxide/graphene matrix using a modified Tollen's test, along with their electrochemical sensor applications. Aside from the single application of Ag NPs, the deposition of Ag NPs on a graphene surface is possible because a graphene sheet is a highly versatile two-dimensional conducting support material and possesses excellent physicochemical properties such as a large theoretical surface area ($2630\text{ m}^2\text{ g}^{-1}$) with high conductivity at room temperature (106 s cm^{-1}), and a wide electrochemical window [27]. Because of the presence of surface functional groups and high conductivity with huge surface area, graphene serves as a support material for growing Ag NPs which is highly beneficial for high-performance electrocatalytic applications.

Herein, we report the controlled synthesis of an rGO-Ag nanocomposite using glucose as a reducing agent in the presence of ammonia and its application towards the electrochemical detection of 4-nitrophenol. Tollens' reaction was modified by introducing rGO support for the controlled growth of Ag NPs and for the synthesis of rGO-Ag nanocomposite. The reaction was monitored at different time duration and the nanocomposite was well characterized at different reaction times (2, 6, 10 and 15 h). The rGO-Ag (15 h) sample-modified GC electrode showed a good sensitivity in SWV with a detection limit of 1.2 nM towards the electrocatalytic reduction of 4-NP. The nanocomposite was stable and selective for 4-NP detection in the presence of its structural analogues such as 2-nitrophenol (2-NP), 2-aminophenol (2-AP), 3-aminophenol (3-AP), 4-aminophenol (4-AP), and 2,4-dichlorophenol (2,4 DCP). The present nanocomposite assay was successfully used for the determination of 4-NP in real water samples.

2. Experimental

2.1. Materials

Graphite flakes were purchased from Asbury Inc. (USA). Silver nitrate (AgNO_3) (98%), and potassium permanganate (KMnO_4) (98%) were purchased from R&M Chemicals. Ammonia solution ($\text{NH}_3\cdot\text{H}_2\text{O}$, 25%) and 4-nitrophenol (4-NP) were obtained from Riedel-de Haen (www.riedeldehaen.com) and Acros Organics (www.acros.com), respectively. Monosodium phosphate (NaH_2PO_4), disodium phosphate (Na_2HPO_4), D-(+)-Glucose (99.5%), sulphuric acid (H_2SO_4 , 98%), phosphoric acid (H_3PO_4),

hydrochloric acid (HCl), and hydrogen peroxide (H_2O_2 , 30%) were obtained from System (www.haioussaintifik.com). All the chemicals were used as received without further purification. Double distilled water was used to prepare the solutions for all the experiments.

2.2. Synthesis of rGO-Ag nanocomposite

GO was prepared by following a simplified Hummer's method [28]. Briefly, 1.5 g of graphite flakes was added into a mixture of 180 mL of concentrated H_2SO_4 and 20 mL of H_3PO_4 under magnetic stirring. To this mixture solution, 9 g of KMnO_4 was added gradually, and the reaction mixture was allowed to stir for three days at room temperature. The mixture was then slowly poured into 50 mL of ice cold deionized water containing 10 mL of H_2O_2 under stirring. The stirring was continued for another 10 min until the solution turned yellow. Finally, the mixture was washed with 1 M HCl and deionized water using centrifugation to remove the metal ions and acid impurities. The rGO-Ag nanocomposite was synthesized as follows. First, 0.75 g of glucose was dissolved in 15 mL of the GO solution (1.0 mg/mL) and stirred for 15 min. To this solution, 10 mL of a $[\text{Ag}(\text{NH}_3)_2]^+$ complex containing 0.06 M AgNO_3 and 0.5 mol L^{-1} ammonia was added and stirred for 15 h. The same procedure was followed to prepare nanocomposites with different reaction times (2, 6, and 10 h). After stirring, the mixture was allowed to sit undisturbed at room temperature for 2 h. The color of the GO changed from brown to muddy green at a reaction time of 15 h, which confirmed the formation of the rGO-Ag nanocomposite. The slurry-like product was centrifuged at 10000 rpm and washed five times with distilled water to remove the impurities. The final product was re-dispersed in 25 mL of distilled water and used for further analyses.

2.3. Electrochemical studies

All the electrochemical experiments were conducted in a three-electrode electrochemical cell system at room temperature. The rGO-Ag nanocomposite modified glassy carbon (GC) electrode was used as a working electrode. Prior to the modification, the GC electrode was polished with alumina slurry ($0.05\text{ }\mu\text{m}$) and cleaned by potential cycling between +1 and -1 V in 0.1 M H_2SO_4 . A platinum wire and a silver/silver chloride (Ag/AgCl) electrode were used as the counter and reference electrodes, respectively. The rGO-Ag nanocomposite-modified GC electrode was fabricated by drop-casting $5\text{ }\mu\text{L}$ of an aqueous rGO-Ag solution onto a GC electrode ($d=3\text{ mm}$) surface and allowing it to dry at room temperature ($25\text{ }^\circ\text{C}$) for 2 h. This rGO-Ag nanocomposite-modified electrode was used for the electrochemical detection of 4-NP. All the electrochemical measurements were performed using a PAR-VersaSTAT-3 electrochemical workstation (www.princetonappliedresearch.com). A N_2 -saturated phosphate buffer (pH 7.2) was used as the supporting electrolyte for the electrochemical experiments. The square wave voltammograms were obtained by applying a step potential of 4 mV, amplitude of 25 mV, and a frequency of 15 Hz unless otherwise mentioned. For real sample analysis, the real water samples were filtered to remove the particulate materials prior to the analysis. Different amounts of 4-NP were added to the real water samples, and the concentration of 4-NP in the spiked water samples was detected using the proposed rGO-Ag nanocomposite sensor.

2.4. Characterization techniques

The absorption spectrum of the rGO-Ag nanocomposite was recorded on a Thermoscientific Evolution 300 UV-visible absorption spectrophotometer. A transmission electron microscopy

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