



Temperature-controlled ethanalamine and Ag-nanoparticle dual-functionalization of graphene oxide for enhanced electrochemical nitrite determination



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ABSTRACT

A highly sensitive and electrochemically active sensor has been fabricated by using an ethanalamine (AE) and Ag-nanoparticle (AgNP) dual-functionalized graphene oxide (fG) architecture (Ag-AEFG). The Ag-AEFG nanocomposites can be constructed via a one-pot hydrothermal method. The AgNPs were uniformly dispersed on the AEFG surface as seen from scanning and transmission electron microscopy. The silver-nanostructure morphology can be controlled via the reaction temperature. The electrochemical properties of the Ag-AEFG-based sensor were investigated by cyclic voltammetry and amperometric techniques. The experimental results indicate that AgNPs act as a catalytic core, AE can be regarded as a reducing agent and the dispersant, AEFG is a conductive platform. The novel sensor exhibits a high sensitivity towards nitrite. The detection limits ($S/N = 3$) for nitrite in phosphate buffer solutions (PBS, pH = 7.4) is 0.023 μM and the linear response range varies from 0.05 to 3000 μM . The novel sensor exhibits a high sensitivity, stability and satisfactory reproducibility. Therefore, it was used to determine the concentration of nitrite in tap water in Nanjing. This study can help us to integrate nanosilver and AEFG for use in advanced electrochemical sensors.

1. Introduction

Nitrite is important in the environment and in ecological systems as an intermediate species in the nitrogen cycle [1,2]. Nitrite is used as a food additive [3], inhibitor [4] and fertilizer [5]. In addition, nitrite is thought to be a precursor in N-nitrosamine production. An excess level of nitrite in the blood yields carcinogens [6,7]. The World Health Organization has reported that the maximum permissible amount of ions in drinking water is 50 mg/L [8]. Therefore, various methods for nitrite detection have been developed, for instance, chromatography [9], spectrophotometry [10], chemiluminescence [11] and electrochemical techniques [12,13]. Among these methods, electrochemical techniques are popular because they are inexpensive, and exhibit a rapid response, and high sensitivity. Nitrite can be involved in electrochemical oxidation and in reduction processes. The greatest merit of electrochemical

detection is to avoid the interference from nitrate and molecular oxygen, because such a technique is based on the oxidation of nitrite.

Various modified electrodes with efficient catalysts, such as metallophthalocyanine [13], porphyrin [14] and metal nanoparticles [15–17], have been developed to improve the selectivity and sensitivity of nitrate determination. Metal nanoparticles, such as Au [18], Pt [19], Pd [20], Cu [21] and Ag [22], have attracted widespread attention because of their unique ability to promote rapid electron transfer [23]. Among them, AgNPs have attracted extensive attention because of their excellent electrocatalytic activity and large surface-to-volume ratio [24]. AgNPs have important application, such as in catalysis [25], surface-enhanced Raman scattering as excellent substrates [26] and DNA sequencing [27], because they are biocompatible and have a low toxicity. The nanomaterial size, shape, morphology and structure are important in modulating electronic and optical properties. To date,

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silver nanoparticles, silver nanowires [28], silver nanosheets [29] and silver nanoprisms [30] have been reported in the literature. Nevertheless, nanoparticle agglomeration has limited their application, and therefore, it is essential to improve the AgNP dispersion when fabricating an electrochemical sensor. Recently, graphene, a fascinating substrate material, has been used to improve the nanoparticle dispersibility because of its nontoxicity, large surface area and high conductivity [31]. Graphene-based sensing materials perform better in electrochemical detection than single graphene or metal nanomaterials because of a synergistic effect, which has resulted in some AgNPs/reduced graphene oxide (GO) sensing systems having been applied in the electrochemical detection fields [22,32–34]. Nitrogen-doped graphene has been confirmed as an excellent platform to enhance electrical conductivities, electrocatalytic activity and wettability [35–37], because nitrogen atom with five valence electrons can form strong valence bonds with carbon atoms [38]. However, the preparation of N-doped graphene usually includes toxic reduction agents, such as hydrazine hydrate, ammonia and sodium borohydride [39,40], and requires complex technology and a higher reaction temperature [41,42].

Our group reported a simultaneous surface and edge functionalization of GO using ethanolamine (AE) through a facile one-step stirring reaction at room temperature based on a nucleophilic addition reaction, amidation and supramolecular self-assembly [43]. AE can be used as an efficient reducing agent and dispersant to functionalize GO. The accurate nanostructures of AE-functionalized GO nanomaterials promote the controlled interfacial engineering of advanced graphene-based nanocomposites. Herein, AE and AgNP dual-functionalized graphene (Ag-AEFG) were fabricated easily and simultaneously by a simple one-pot hydrothermal method. The reaction temperature influences the nanosize and distribution of AgNPs on the AEFG surface. GO cannot be coated by AgNPs without AE addition, and is accompanied by the preservation of a GO nanostructure. Ag-AEFG exhibits better conductivity, electrocatalytic activity, and wettability than rGO/Ag materials due to its nitrogen atom doping. This is because the nitrogen atom can decarbonize to form a stronger chemical bond. Most importantly, an electrochemical sensor that is based on Ag-AEFG exhibits an enhanced performance for nitrite detection, which indicates the efficient synergistic effect for a high sensitivity, stability and satisfactory reproducibility. The sensor was used to determine the concentration of nitrite in tap water.

2. Experimental

2.1. Synthesis of Ag-AEFG composite

Graphite oxide (GO) was prepared by a modified Hummers method [44]. The Ag-AEFG composite was prepared via a facile one-pot hydrothermal method. Briefly, 50 mg GO was dispersed in 10 mL water to yield uniform dispersion by ultrasonication for 7 h. Next, 10 mL AgNO₃ aqueous solution (0.01 M) was added into as-prepared GO suspension by sonification for 0.5 h. Then the obtained suspension was transferred into a 50 mL Teflon-lined autoclave, and 1 g ethanol amine (AE) dissolved in 19 mL water was added into the suspension rapidly. Finally the mixture was sealed and heated at 80 °C for 10 h. After cooled to room temperature naturally, the precipitation was collected and washed thoroughly with ultrapure water and ethanol for three times, and dried in a vacuum oven at 60 °C for 12 h. The construction process of the Ag-AEFG is showed in Scheme 1. Three different types of products were prepared by the same method at the different reaction temperatures of 100, 120 and 140 °C, respectively. For easy expression, Ag-AEFG100 represents the product prepared at 100 °C. In order to verify the reducibility of AE, we also chose the optimized reaction temperature (100 °C) to prepare the product, named as so-called Ag-GO, the other conditions are the same, except that no AE was added.

3. Results and discussion

3.1. Characterization of Ag-AEFG nanocomposite

The X-ray diffraction (XRD) patterns of pure GO and Ag-AEFG at different temperatures are shown in Fig. 1a. The typical sharp diffraction peaks at $2\theta = 10.7^\circ$ of the GO are consistent with the specific crystal diffraction of the graphite oxide. The disappearance of this peak in Ag-AEFG shows that the GO has been reduced partially. Ag-AEFG nanocomposites that are prepared at the four different temperatures show the similar patterns. The sharp crystal diffraction peaks at 38.1° , 44.3° , 64.4° and 77.4° correspond to the (111), (200), (220) and (311) planes of a face-centered cubic Ag pattern (JPCDS 65–2871). The results confirm that the assumption of AE as a reducing agent. The highest relative intensity of the diffraction peaks of Ag-AEFG100 indicates that this nanocomposite has the highest crystallinity and few lattice defects. Fig. 1b shows the Fourier transform infrared (FT-IR) spectra of the GO, Ag-AEFG80, Ag-AEFG100, Ag-AEFG120 and Ag-AEFG140. In the FT-IR spectrum of the GO, the peaks at 3396, 1632, 1075 and 1720 cm^{-1} are ascribed to O–H (stretching vibration), O–H (bending vibrations), C–O–C (stretching vibration) and C=O (stretching vibration) groups [43], which indicates that GO was prepared successfully. In the spectra of the Ag-AEFG nanocomposites, the corresponding peak intensities of the oxygen-containing functional groups are weakened and even disappeared, which demonstrates the reduction of GO. The appearance of the new peaks at 2990 and 2896 cm^{-1} results from the characteristic peak of $-\text{CH}_2-$ of AE in the curve of the Ag-AEFG nanocomposites compared with GO, which indicates that AE can reduce GO and achieve AE functionalization of GO [43]. The C–O–C stretching adsorption peak of Ag-AEFG shifted from 1075 to 1056 cm^{-1} , which confirmed the introduction of aliphatic C–N bonds. In addition, a nitrogen-related peak appeared at 1558 cm^{-1} in the spectrum of Ag-AEFG owing to N–H bending bonds. The peak at 1733 cm^{-1} from the carbonyl stretching peak of the carbonyl groups in GO decreased significantly in the nanomaterials, which may be explained by the COOH groups in GO reacting with NH₂ in AE to generate new chemical bonds, such as carboxylate ($\text{R}^1\text{COONH}_3\text{R}^2$) and amide (R^1CONR^2). A new band at 1558 cm^{-1} that was assigned to a carboxylic acid salt (COO⁻) asymmetric stretch mode is observed. This could testify to the existence of a RCOONH₄ structure [43]. The lattice defects and the degree of chaos of the materials were characterized by D and G bands at ~ 1300 and 1580 cm^{-1} in the Raman spectra. As shown in Fig. 1c, the intensity of the D band corresponds to a degree of disorder of the carbon material, and represents the lattice defect of the C atom. The intensity of the G band represents the strength of the in-plane stretching vibration of the C atom sp^2 hybrid type. Therefore, the intensity ratio of the D band and G band (I_D/I_G) can be used to characterize the degree of disorder. Fig. 1c shows the Raman spectra of the GO and Ag-AEFG that were prepared at different temperatures, respectively. The I_D/I_G values of the GO and Ag-AEFG at 80, 100, 120 and 140 °C are 1.02, 1.06, 1.10, 1.15, 1.22, respectively. This observation indicates the reduction of GO and the formation of AE-functionalized graphene. The highest ratio value for Ag-AEFG illustrates the best modification degree. The skeleton structure GO remains in the Ag-AEFG after functionalization. All the results correlate with the XRD results.

X-ray photoelectron spectroscopy (XPS) is not a valid method to achieve the qualitative analysis of chemical elements, but is an effective method to investigate the electronic structure and chemical bond structure. Fig. 1d shows the XPS spectra of GO and Ag-AEFG100. The existence of N1s and Ag 3d peaks proves the successful reduction and modification of GO with the aid of AE. Therefore, Ag⁺ can be transferred to Ag nanoparticles onto the surface of reduced graphene. This observation is consistent with the XRD and FT-IR results. The high-resolution C1s XPS spectrum of GO (Fig. S1) shows four peaks, C–C (284.4 eV), C–OH (285.1 eV), C–O–C (286.3 eV) and C (O)–O (288.6 eV), respectively [43]. Typically, the Ag-AEFG100 exhibits one

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