Determination of nitrite in tap water: A comparative study between cerium, titanium and selenium dioxide doped reduced graphene oxide modified glassy carbon electrodes

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ABSTRACT

In this work, a comparative study between three different novel synthesized materials, cerium, titanium and selenium dioxide doped reduced graphene oxide, was done toward detection of nitrite in tap water. It was found that best response and analytical performance were achieved with acerium dioxide reduced graphene oxide modified glassy carbon electrode. The materials were synthesized and characterized with transmission electron microscopy (TEM), electrochemical impedance spectroscopy and UV–vis spectroscopy. The prepared electrode has a wide linear range from 0.7 to 385 μM with a detection of 0.18 μM using amperometric detection. Various parameters were optimized and the sensor was successfully applied for the nitrite ion quantification in tap water samples. Inclusion of different dopants in the graphene structure for novel materials to modify solid electrodes was found to enhance the catalytic effect toward nitrite detection.

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1. Introduction

Nitrite salts of different metals are naturally present in environment, natural water and in food. Nitrites have found wide application in various industries. In food production nitrites are usually used as food preservative (E250) and in others fields of industry nitrites are used for inhibition of corrosion processes in big water industrial units [1–4]. These salts are present in the soil, sometimes in high quantity, which can cause their presence in high level in natural waters [3]. The potential metabolites of nitrite could be *N*-nitroso compounds, which possess carcinogenic effect [4–6]. Nitrites also can cause different health implications such as gastric and nasopharyngeal problems when people are seriously exposed [7–9]. Due to these facts a development of a fast, simple, cost-effective, selective and sensitive method for its quantification is very important. Numerous methods have been reported in the literature dealing with nitrites quantification, such as spectrophotometric methods [10,11], flow methods [12], chemiluminescence [13] as well as electroanalytical methods [4,14–22].

Electroanalytical methods offer all advantages of one analytical procedure to be promising for quantification of species present in the environment. Different solid electrodes, now widely used, are manufactured from materials such as platinum, silver, gold and different types of carbon. However, they possess some disadvantages such as passivation of the surface and notable background currents, and due to these facts in recent years chemically modified electrodes are still gaining ground in electroanalysis [23–25]. A proper selection of the electrode material can strongly improve important parameters for the electroanalytical procedure, such as sensitivity, selectivity and background current.

Recently the application of reduced graphene oxide decorated with differentnanomaterials has been reported for the detection of various analytes from the environment, food and biological fluids [16,25–28].Titanium dioxide in combination with reduced graphene oxide and copper was reported by Hasan et al. for the photoelectrochemical reduction of CO_2 [29], as well as for dopamine sensing [30]. Due to date, there is no data about possible application of cerium dioxide and selenium dioxide doped reduced graphene oxide.

In this study, we aimed to investigate theapplication of novel synthesized materials based on reduced graphene oxide for the quantification of nitrite in water.The introductionof different oxide materials in the reduced graphene oxide structure showed to

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improve its characteristics especially with respect to sensitivity and selectivity. Important parameters for the analytical procedure have been optimized and successfully applied for nitrite ion detection in tap water.

2. Experimental

2.1. Reagents

Highly pure water (resistivity >18 MΩ cm, MilliQ, Millipore) was used for the preparation of all solution used in this study. Analytical grade reagents were used. They were obtained from Sigma Aldrich (if not stated otherwise) and used as received without further purification. Britton-Robinson buffer solution (BRBS) was prepared by mixing boric acid, acetic acid and phosphoric acid in the concentration of 0.04 M. Graphene oxide was purchased from ACS Materials.

2.2. Apparatus

All electrochemical measurements were done with a potentiostat/galvanostat (Autolab PGSTAT 302N, Metrohm Autolab B.V., The Netherlands) controlled by the corresponding electrochemical software (Nova 1.9). The electrochemical cell with a total volume of 10 mL was equipped with a glassy carbon (GC) working electrode (plain or modified), an Ag/AgCl (saturated KCl, all potentials reported in this paper are referred versus this electrode) as the reference and a Pt wire as the counter electrode. All measurements were done at an ambient temperature. The pH of the BRBS was adjusted with 0.5 M sodium hydroxide using an Orion pH meter (model 1230) equipped with a combined glass electrode. UV–vis absorption spectra were recorded by using a VARIAN spectrophotometer in the wavelength range from 200 to 800 nm. The structure and chemistry of the samples were studied using a 200-kV transmission electron microscope (TEM; JEM-2100, Jeol Inc.) equipped with a LaB6 filament and an energy-dispersive X-ray spectrometer (EDS). The micrographs were recorded with a high-resolution slow-scan CCD camera (Orius DC1000, Gatan Inc.). Powdered synthesized samples were dispersed in DMF, while GO was dispersed in water, and transferred onto commercially available Cu grids (200 mesh Cu holey carbon, SPI Supplies/Structure Probe, Inc.).

For cyclic voltammetry the potential was swept in the range of 0–1.5 V at the scan rate of 50 mV/s (if not stated otherwise) and this was used for selection of pH of the supporting electrolyte as well as for the investigation of the nature of the electrochemical reaction at the new electrode surface. For detection of nitrite ion as an electrochemical technique, amperometry was selected. All amperograms were recorded at a constant potential of +1.0 V, which is selected from previous measurements. The limit of detection (LOD) was calculated according the equation:

$$LOD = 3 \, x\sigma_{intercept}/slope.$$

2.3. Synthesis of the electrode materials

Novel materials were synthesized by modifying the previously described procedures for synthesis of similar materials [26–28]. According to these procedures the metal oxide is produced *in situ* on the surface of graphene oxide, followed by reduction of such hybrids. In the procedure here the metal oxides were directly added to a solution containing graphene oxide and such hybrids were reduced by glucose and Zn foils. All three selected doping materials for reduced graphene were tetravalent oxides of metals, titanium, cerium and selenium, abbreviated as TiOrGo, CeOrGo and SeOrGo, respectively. In 5.0 mL of graphene oxide suspension with
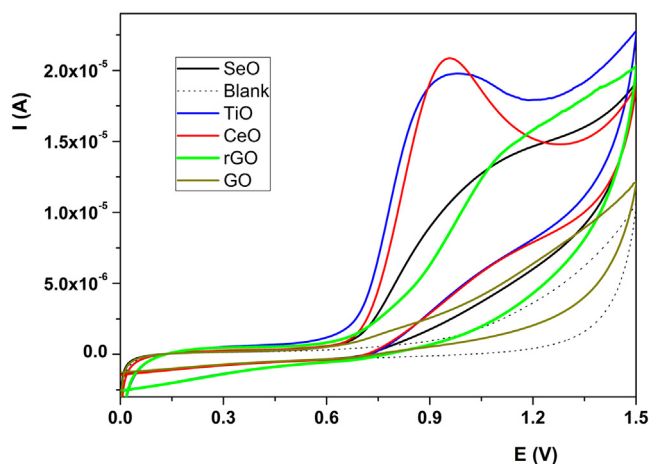

Fig 1. Electrochemical response in absence (dotted line) and presence (solid lines) of 1 mM of nitrite ion at various modified GC electrode in BRBS at pH 4.2, scan rate 50 mV/s.

a concentration of 1 mg/ml (this suspension was ultra-sonicated for 3 h before use) a 2.3×10^{-4} M of metal oxide was added and ultra-sonicated for more 2 h. After that 50 mL of glucose solution (2000 ppm) were added together with Zn foils and heated for 30 min at 75 °C with continuous stirring. After cooling the suspension to room temperature followed by removal of Zn foils the obtained material was collected by centrifugation, washed three times with water and dried. For comparison the reduced graphene oxide without dopant (metal oxide) was prepared following same procedure.

2.4. Preparation of the modified electrodes

The obtained crude materials were weighed, suspended in DMF (dimethylformamide) to a of 8 mg/ml and ultra-sonicated for 1 h. It was found that this concentration provides best response for nitrite oxidation (data not shown) and was used in all further experiments. The surface of glassy carbon electrode was polished with 0.3 and 0.05 μm alumina powder, washed with water and sonicated for 10 min in nitric acid followed by washing with water. Then 10 μL of the suspension was pipetted on the electrode surface and dried at room temperature. Before use, the suspensions were ultra-sonicated for 1–2 h. Hand mixing or vortexing did not provide satisfactory results.

3. Results and discussions

3.1. Electrochemical behavior of the modified electrodes

The cyclic voltammograms of nitrite in BRBS at pH 4.2 show that highest current was obtained cerium dioxide/reduced graphite oxide(CeOrGo, Fig. 1). The increase in the current obtained with CeOrGo, calculated after background current subtraction is around 100% in comparison with rGo and SeOrGo, and around 30% compared to TiOrGo. From Fig. 1, it can be concluded that the other electrodes do not show well-defined and oval-shaped peaks for the nitrite oxidation. These results can be correlated with UV–vis spectra of all materials which are presented in Fig. 2A. It is obvious that when SeO$_2$ was used as a dopant there is no change in the absorption spectra in comparison with reduced graphene oxide. In case of titanium and cerium dioxide doping a high decrease in the visible part of spectra is observed, which is attributed to the presence of dopant in material structure. A strong decrease of absorbance is correlated with inclusion of metal oxides in the reduced graphene structure