

Reduced Graphene Oxide in the Construction of Solid-State Bromide-Selective Electrode

N. V. Shvedene*, A. V. Rzhavskaia, N. M. Anuchin, O. O. Kapitanova, A. N. Baranov, and I. V. Pletnev

Department of Chemistry, Moscow State University, Moscow, 119992 Russia

*e-mail: shvedene@gmail.com

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Abstract—To improve the electrochemical performance of solid-state printed electrodes, reduced graphene oxide is used as an intermediate layer (mediator) between the surface layer of a current collector and the ionophore layer. A graphene oxide film was deposited onto the surface of printed electrodes by drop-casting, followed by reduction and electrochemical deposition. An ionic liquid 1,3-dihexadecylimidazolium bromide served as ionophore. The effect of reduced graphene oxide on the characteristics of the ion-selective electrode is studied, and it is shown that the sensors electrochemically modified with reduced graphene oxide have the best performance. These sensors exhibit a stable, well-reproducible response to bromide ions with the slope of the electrode function close to the Nernstian value (-60.7 ± 0.7 mV/dec) and a low detection limit of 3.6×10^{-6} M. The response time for all of the electrodes does not exceed 15 s even in dilute solutions.

Keywords: solid-state ion-selective electrode, reduced graphene oxide, ionic liquid

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Ion-selective electrodes (ISEs) are among the most widely used chemical sensors for solving contemporary analytical problems because of their accessibility, portability, low cost, and the possibility to analyze samples without long-term sample preparation. To date, more than one hundred different ions can be determined using ISEs; sensors exhibit response to the analyte in a wide concentration range, which is typical for a very limited number of analytical methods [1]. Among ISEs, entirely solid-state electrodes attract particular attention. These include the electrodes of the coated wire type, in which the ion-sensitive membrane is applied onto a metallic conductor [2]. Most often, the ion-sensitive membrane is a polymer matrix, into which an ionophore is introduced [3]. Unfortunately, coated wire electrodes have low service life and low stability of potential due to the blockage of signal transmission from the membrane to the collector, that is, because the smooth transition from ionic conductivity in the membrane to electron conductivity in the collector is disturbed [4]. Therefore, such ISEs have received neither wide recognition nor practical application.

Several conditions are found to increase the stability of the ISE potential [5]. The authors believe that the most important factor is to ensure the equilibrium and stable transition from ionic to electronic conductivity. This problem can be solved by the use of a material with suitable ion-exchange properties as an intermediate layer between the electron-conductive cur-

rent collector and the ion-conductive membrane. The introduction of electroactive polymers such as polyaniline, polypyrrole, and poly(3-octylthiophene) in the electrode intermediate layer appeared to be rather promising, since these additives significantly increased the stability of the sensor by accelerating the charge transfer from the corresponding surfaces [5–7]. However, in the operation of solid-state ISEs prepared using conductive polymers, some disadvantages have been revealed. These include the sensor sensitivity to light and the formation of a water film between the membrane and the conductive polymer [8, 9], which leads to significant deterioration of the sensor performance. That chemical and photochemical sensitivity of conductive polymers stimulated the search and study of other transducers for the conversion of ionic conductivity to electronic conductivity. Various derivatives of carbon, for example, carbon nanotubes [10], fullerenes [11], and nanostructured carbon [12], were proposed for this purpose.

Graphene is also a promising carbon material; it represents a two-dimensional allotropic form of carbon, formed by a layer of sp^2 -hybridized atoms. Graphene has a high mobility of charge carriers (2×10^5 cm²/(V s) [13]), and its thermal conductivity (5×10^3 W/(m K) and strength ($E > 10^{12}$ Pa) are record high [14]. Not only graphene layers, but also graphene oxide (GO) or reduced graphene oxide (RGO), which may contain two-dimensional, one-dimensional, or zero-dimensional graphene in the form of clusters or

quantum dots in the oxide matrix, are of practical interest. Graphene oxide can be reduced to a highly conductive state by chemical or electrochemical methods [15–17]. Reduced graphene oxide is a promising material for electroanalytical chemistry because of its relatively high thermal conductivity (2400 S/m [17]), the electrocatalytic activity [18], hydrophobicity, mechanical strength ($E > 10^8$ Pa [19]), and chemical stability [17].

Attractive physicochemical properties and relatively simple method for synthesis of RGO and GO determine its use in the development of electrochemical sensors and biosensors [20, 21]. The examples of the use of RGO in voltammetry as a surface modifier of glassy carbon or graphite electrodes in the study of the electrocatalytic activity of compounds and in the creation of biosensors and immunosensors are numerous [22–24]. The modification with graphene improves the sensitivity of the biosensor to an analyte substrate and enables the detection without prelabeling and without the use of mediators.

Due to its high conductivity and the developed specific surface area, RGO can serve as a transducer from ionic to electronic conductivity in creating solid-state potentiometric sensors. In the past two years, the articles on the use of graphene and its derivatives to improve the performance of solid-state ISEs have been published [25–35]. According to the literature, the electrochemical characteristics of ISEs, such as detection limit, response time, and reproducibility of potential, are improved due to increased stability of signal transmission. A glassy carbon electrode or a carbon-paste electrode is most often used as a conductive material in the construction of such ISEs. The characteristics of solid-state ISEs prepared using polyaniline and graphene are compared, and the advantages of the latter due to the absence of photo- and chemical sensitivity are demonstrated [27]. A composition of graphene and iron oxide nanoparticles as a conductive layer of a lanthanum(III) selective electrode is proposed, which, in addition to optimal electrical and magnetic properties, possesses high absorption capacity [32]. An ISE for nitrate ions was studied, based on a glassy carbon electrode with the use of RGO as a mediator of the transition from ionic to electronic conductivity [34]. Methyltridodecylammonium nitrate was used as an ionophore.

The developed ISE exhibits a stable response to nitrate for a long time, which indicates the absence of the water layer between the membrane and the current collector. However, the proposed ISE yielded a high detection limit, which restricts its use in the analysis of real samples. Note that almost all publications are devoted to the creation of ISEs for metal cations (potassium, calcium, zinc, or copper) using the corresponding ionophores. Coated-wire ISEs are one of the types of solid-state electrodes. The study and use of these electrodes opened the prospect for a variety of miniature sensors. The ISEs based on planar printed

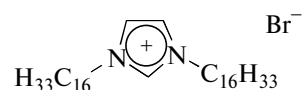
electrodes can be attributed to this type of electrodes. Miniaturization of ISEs decreases the cost and duration of analysis, enables the performance of tests outside the laboratory, and gives the possibility to organize mass production. To date, only one article is found, in which a calcium-selective electrode is proposed, prepared on the basis of a printed electrode, where RGO is used as a mediator [35]. In our laboratory, solid-state sensors based on planar printed electrodes using ionic liquids (ILs) as active components of the membrane are being developed [36–38].

In this paper, the possibility of using graphene oxide to improve the characteristics of the printed ISE for bromide ion with a membrane based on the ionic liquid 1,3-dihexadecylimidazolium bromide is studied [39].

EXPERIMENTAL

Reagents. Graphene oxide was synthesized by a modified Hammers method [40]. To study the potentiometric response of membranes, a solution of KBr was prepared by dissolving an accurately weighed portion of KBr (analytical grade or better) in distilled water; solutions with a lower concentration were obtained by serial dilution.

As an ionophore we used ionic liquid 1,3-dihexadecylimidazolium bromide ($T_{m.p.} = 78^\circ\text{C}$)



Preparation of a solid-state electrode. Planar screen-printed electrodes from Elcom and Rusens (Russia) with an indicator surface based on graphite paste were used. The surface of the printed electrode was modified by a GO film by two methods. An ethanol solution of GO (0.1 mg/mL) was applied to the electrode by the drop casting method, followed by chemical reduction. After the drop was dried, the electrode was treated with a solution of ascorbic acid (3 mg/mL) and held in an oven at 95°C for 15 min. Thereafter, the electrode surface was washed with distilled water to remove excess reducing agent and its oxidation products [15]. Graphene was electrodeposited onto the surface of the printed electrode in accordance with guidelines [41]. The cell equipped with the printed indicator electrode, a platinum auxiliary electrode, and a silver–silver chloride reference electrode was filled with an aqueous solution of graphene oxide (1.0 mg/mL) and a borate buffer solution at pH 9.18. In order to create an inert atmosphere, nitrogen was continuously passed through the cell. The cell voltage was in the range of potentials from -1.5 to $+0.7$ V with the potential sweep rate of 50 mV/s; the number of cycles was 10. Then, the ionophore (ionic liquid; ~ 0.5 mg) was applied on the surface of the obtained electrodes and melted for 5–10 s over an electric hot

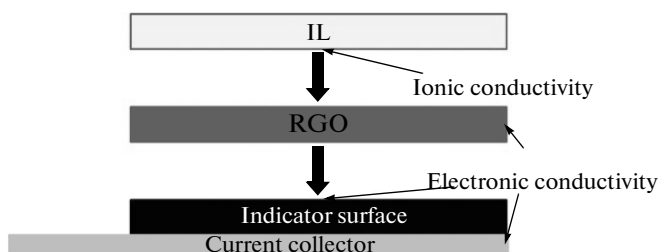


Fig. 1. Construction of a solid-state electrode.

plate. After 2–3 min of cooling at room temperature, the electrode was ready to use (Fig. 1).

Apparatus and experimental procedures. The morphology of the samples obtained on the surface of the printed electrode was examined using a Supra 50VP (LEO) scanning electron microscope. Raman spectra of graphene and graphene oxide were recorded using a Renishaw Raman Microscope. Lasers with wavelengths of 514 and 633 nm was the excitation source. The spectra were recorded at room temperature. The spectral resolution of the Raman spectrometer was 1 cm^{-1} .

For the electrochemical deposition of RGO using cyclic voltammetry, a potentiostat from PalmSens (Netherlands) was applied. Potentiometric measure-

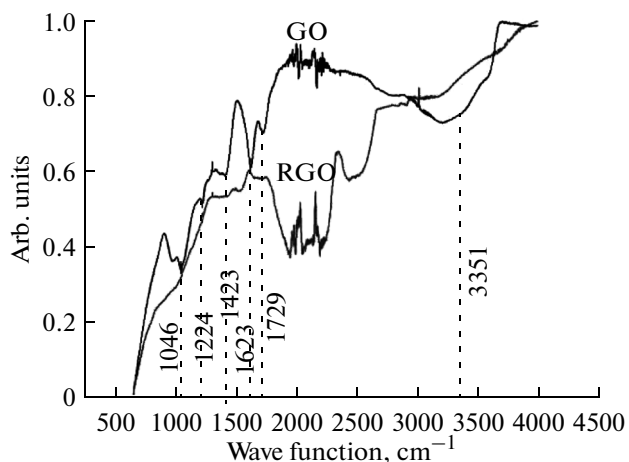


Fig. 2. IR spectroscopy data of graphene oxide and reduced graphene oxide.

ments were performed using an Ekspert-001 potentiometer (Econix-Expert, Russia). The resulting electrodes were used for measuring the potential immediately after modifying their working surface. The electrochemical properties of the prepared solid-state ISE were studied by measuring the emf of galvanic cell.

Indicator surface of the planar electrode (graphite paste)

RGO

Ionic liquid

Test solution

AgCl/Ag

The slope of the electrode function was determined by least squares method; the detection limit was found using the “ c_{\min} ” program based on the recommendations of the IUPAC [42].

RESULTS AND DISCUSSION

Investigation of reduced graphene oxide. Infrared spectra of GO before and after the reduction with ascorbic acid are presented in Fig. 2. The bands indicated in Fig. 2 are responsible for the concentration of oxygen in the substance. The bands at 1046, 1224, and 1729 cm^{-1} correspond to the stretching vibrations of oxygen in groups C–O, C–OH, and C=O, respectively. The band at 1423 cm^{-1} corresponds to the characteristic vibrations of C–O. The band at 1623 cm^{-1} is responsible for the vibrations of adsorbed water. The band at 3351 cm^{-1} is responsible for the vibrations of O–H [43]. It is seen that after the reduction, the intensity of the bands responsible for the vibrations of oxygen-containing functional groups is considerably declined.

We also recorded the Raman spectra of obtained substances (Fig. 3). It is seen in the figure that the presence of peak *G* (1600 cm^{-1}), corresponding to vibrations of neighboring carbon atoms in the graphite matrix, is characteristic of all the spectra of GO. It is obvious that in both original GO and resulting RGO, the intensity of peak *D* (1350 cm^{-1}), responsible for the defects in the carbon structure, is significantly higher than in the case of the electrochemically reduced GO (ERGO). Defects are both various oxygen-containing functional groups, present in graphene oxide, and possible fractures of the hexagonal structure appearing during the oxidation and splitting of graphite. In the case of ERGO, the lowering of peaks *D* and *G* indicates the restoration of the original graphite matrix.

The morphology of the obtained particles was studied using data from a scanning electron microscope. The photographs of the GO films on the surface of the printed electrode are presented in Fig. 4. It is seen that a continuous film was obtained; irregularities are caused by the initial roughness of the carbon substrate.

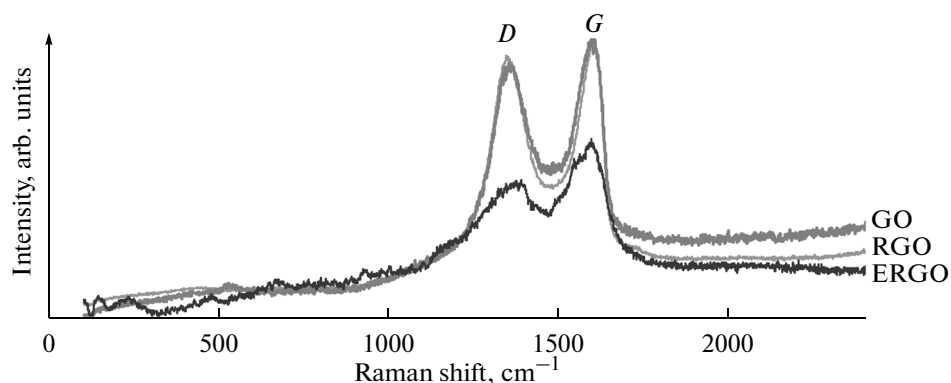


Fig. 3. Raman spectrum of the original graphene oxide and graphene oxide reduced by the chemical and electrochemical methods.

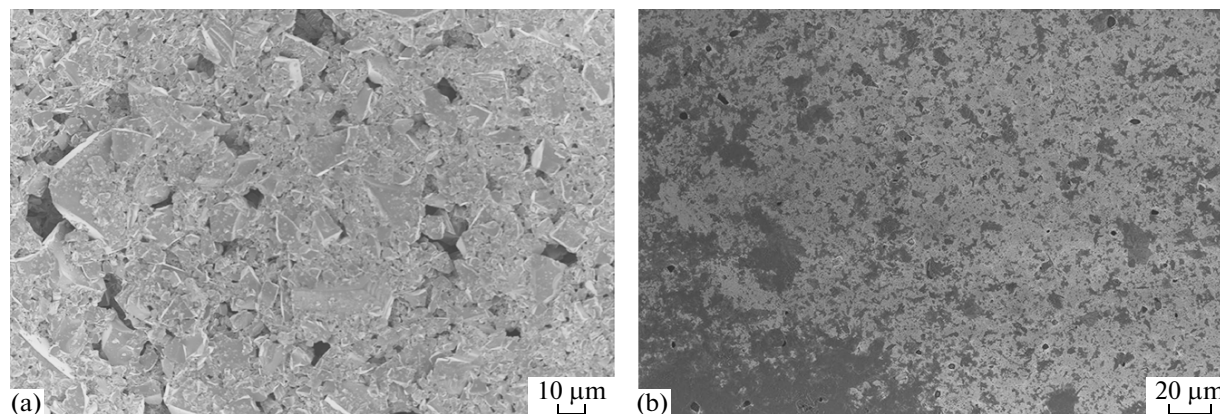


Fig. 4. Scanning electron microscope image of the surface of the printed electrode (a) without and (b) with a deposited film of electrochemically reduced graphene oxide.

Application of RGO as a mediator of the transition from ionic to electronic conductivity in the solid-state ISE.

Previously, we found that the printed electrode modified with 1,3-dihexadecylimidazolium bromide exhibited a reproducible Nernstian response to bromide ion [39]. However, the detection limit of this sensor is quite high, and the stability of the sensor decreases over time. It is known that graphene and its derivatives, introduced in the intermediate layer of ISE, improve the electrochemical performance of the electrode by providing a smooth transition from ionic to electronic conductivity. It was interesting to study the effect of RGO on the functioning of solid-state ISE and compare characteristics of the obtained sensors.

The potentiometric response of electrodes containing RGO, obtained by chemical reduction, is studied. This solid-state electrode demonstrates the response to bromide ion slightly above the Nernstian value. The slope of the electrode function is $-(67 \pm 1)$ mV/dec; the response time does not exceed

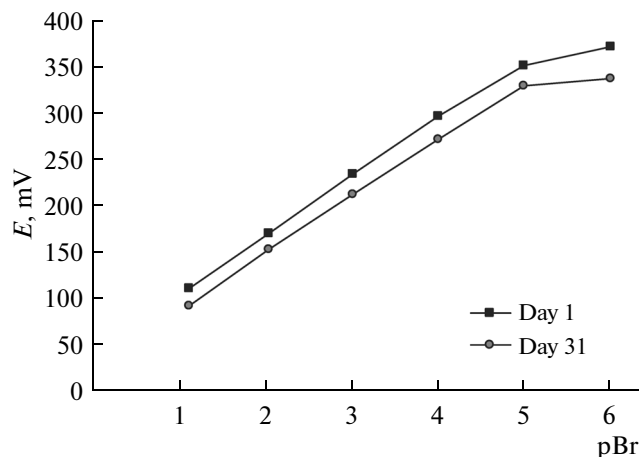


Fig. 5. Electrode function of the sensor with electrochemically reduced graphene oxide, modified with IL, in a bromide solution measured in different days.

Performance characteristics of the electrodes with GO and RGO ($n = 5$, $P = 0.95$)

Characteristic	IL only [39]	IL + RGO	IL + ERGO
Response slope, mV/dec	-58.5 ± 0.7	-67 ± 1	-60.7 ± 0.7
c_{\min} , M	1.6×10^{-5}	4.2×10^{-6}	3.6×10^{-6}
Linearity range, M	10^{-4} – 10^{-1}	10^{-5} – 10^{-1}	10^{-5} – 10^{-1}
Response time, s	15	15	15

15 s (10^{-4} M); the detection limit is 4.2×10^{-6} M. It should be noted that the sensitivity and reproducibility of the sensor measurements remains virtually unchanged for 30 days of operations. A disadvantage of the chemical methods is the uneven distribution of graphene oxide over the electrode surface due to the spreading of the drop, which leads to that the thickness of the GO film cannot be controlled.

Another way to obtain RGO is its electrodeposition, which was carried out by cyclic voltammetry. In this case, it becomes possible to optimize the reduction process by varying the number of cycles and the concentration of solution. In addition, the obtained film is thinner and more uniform in thickness.

The electrode with RGO, obtained by the voltammetric technique, demonstrates the slope of the electrode function close to the theoretical value, that is, $-(60.7 \pm 0.7)$ mV/dec (Fig. 5). The response time is less than 15 s even in dilute solutions; the detection limit is 3.6×10^{-6} M.

It can be noted in the comparison of the obtained electrodes modified with IL without RGO and with applied RGO that the introduction of RGO improved the electrode performance (table). In particular, the detection limit for the bromide ion was decreased, the range of linearity of electrode function was expanded, and the slope of electrode function in the case of IL + RGO was higher than the Nernstian value but well reproducible over time. The response time remained the same.

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