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Carboxylated graphene as a sensing material for electrochemical uranyl ion detection

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ABSTRACT

The present study is focused on the application of graphene modified with carboxylic groups in the development of sensor for electrochemical detection for uranyl ion. After the graphene synthesis and its characterization, the optimization of the measurement conditions and working parameters of sensors were evaluated. Uranyl ion concentration was determined with the use of voltammetric techniques by comparison of current change of redox indicator hexaammineruthenium(III) chloride. The prepared sensor demonstrated linear response within the range of 5×10^{-8} to 5×10^{-6} mol L^{-1} and significant selectivity towards ${UO_2}^{2+}$ ions over other examined cations (e.g. Cd^{2+}, Ca^{2+}, Sr^{2+}, Co^{2+}, Mg^{2+}, Pb^{2+} and for Fe^{3+}).

1. Introduction

Since its discovery, graphene draws great attention of scientists all over the world and still is one of the most intensively studied materials [1]. This is a crystalline 2-dimensional allotrope of carbon characterized with specific combination of properties like high specific surface area of 2630 m^2/g, being the gapless semiconductor, remarkable electron mobility at room temperature (15000 $cm^2 V^{-1} s^{-1}$), resistivity of 10^{-6} Ω cm, large thermal conductivity of approximately 5300 $W m^{-1} K^{-1}$ or optical transparency, in addition to flexibility, robustness and environmental stability [2]. Because the above, the possible graphene utilization was investigated in many fields of applications like biological engineering [3], optical electronics [4], ultrafiltration [5], composite materials [6] or photovoltaic cells and energy storage [7].

The graphene and graphene derivatives were used also for water purification e.g. as sorbent for nickel [8], ^{129}I [9], lead [10], mercury [11] or as the sorbent for separation and preconcentration of ultra-trace amounts of gold ions from water samples [12]. To make the sorption possible in each of above mentioned case, the graphene or graphene oxide was additionally modified with e.g. silver nanoparticles [11], magnetic particles formed form Fe(II) and Fe(III) [12], EDTA- and amine-functionalized [8] or chitosan/FeOOH nanocomposite [10]. Since the specific affinity of this 2D carbon material to different chemical species was confirmed, it was also used as a sensing material in analytical chemistry applications [13]. Functionalized graphene or graphene composites were the basis for fabrication of various kinds of electrodes dedicated to detection of a wide range of chemical and biochemical species, such as H_2O_2 [14], dopamine [15], ascorbic acid [16], glucose [17], DNA [18] or antigens [19]. In the case of the compounds with the higher molecular weight (like DNA or antigens) the recognition part was built with nucleic acids [17] or antibodies [18]. As can be found in the literature, graphene composites possess strong affinity also to inorganic compounds e.g. uranyl ion [20]. As the uranium is one of the essential elements in nuclear energy programs, a component in the production of tank armor and armor piercing ammunition, a dye in staining of ceramic products as well as in electron microscopy investigations of biological samples, it has been inevitably released into the environment and would cause serious health problems due to its extremely chemical and radioactive toxicity [21]. According to literature, uranyl ion exhibits affinity to graphene oxide [20]. Authors stated that the U(VI) sorption on such a material is rapid, strongly dependent on pH, attaining a plateau at pH 4.0–7.5, and independent of the ionic strength. As was shown by the authors the crucial role in the sorption play oxygen-containing functional groups of GO (oxidized graphene sheets modified mostly with epoxide and hydroxyl groups in addition to carbonyl and carboxyl groups located presumably at the edges). The maximum sorption capacity of GO for U(VI) (299 mg/g at pH 4.0) makes GO one of the most effective sorbents reported for U(VI) so far. At higher pH values the functional groups of GO are

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deprotonated and the surface gains negative charge, so negatively charged uranium species are repulsed from GO surface and as the consequence the adsorption ability is decreased and finally lost. The ionic strength independence of the sorption is attributed, according to the authors, to the formation of inner-sphere surface complexes of metal ions. Authors investigated also the local atomic structure of U(VI) adsorbed on GO with the use of EXAFS spectroscopy [20]. Changes in the registered spectra resulting from changes in the pH of the samples confirmed gradual structure transformations of U(VI) adsorbed on GO. Because $UO_2{}^{2+}$ is a hard Lewis acid, it possess a strong affinity for oxygen-containing donor ligands [20]. The GO characteristics, like the abundant oxygen-containing functional groups on its sheets surfaces, leads to formation of a stable inner-sphere complexes with $UO_2{}^{2+}$ rather than simple physical sorption of $UO_2{}^{2+}$. This concerns only the above mentioned optimum pH range. Spectrum registered for the pH 7.6 indicating surface precipitation of U(VI) (where the prevalent ion form is $UO_2(OH)_3{}^-$ [22]) onto the GO surface [20]. Further, theoretical studies of Qun-Yan Wu et al. [23] applying density functional theory (DFT) combined with quasi-relativistic smallcore pseudopotentials concerned optimization of 22 complexes between uranyl ion and GO. Authors investigated oxygen-containing functional groups like hydroxyl, carboxyl, amido, and dimethylformamide. They observed that the formation of hydrogen bonds in the anionic complexes uranyl/$GO^{-/2-}$ complexes can enhance the binding ability of anionic GO toward uranyl ions. Moreover, the thermodynamic calculations showed that the changes of the Gibbs free energies in solution were relatively more negative for complexation reactions concerning the hydroxyl and carboxyl functionalized anionic GO complexes [23].

The interesting results of such an extensive research concerning interactions between graphene oxygen-containing functional groups and uranyl ion seems to be worth to investigate this material as the sensing layer in electrochemical sensors. As the results, the presented study is dedicated to the novel application of carboxylated graphene. To our best knowledge this is the first time when such a graphene species is used as the electrode material in electrochemical uranyl ion detection system.

2. Material and methods

2.1. Apparatus

Voltammetric studies were performed with a CHI 660A and CHI 1040A electrochemical workstations (CH Instruments, USA). Electrochemical impedance measurements (EIS) were carried out with a CHI 660A electrochemical workstation (CH Instruments, USA). The measurements were recorded with a conventional three-electrode system including a glassy carbon disk electrode (CH Instruments, USA), an Ag/AgCl/1.0 mol L^{-1} KCl reference electrode and a gold wire auxiliary electrode. All potentials are measured versus Ag/AgCl reference electrode at room temperature. EIS was conducted at a dc potential of 200 mV and the ac amplitude was 5 mV for the frequency range of 1 Hz–100 kHz. The cyclic voltammetry was performed at a sweep rate of 100 mV s^{-1}, while the square wave voltammetry was conducted at a pulse amplitude of 25 mV, increment of 4 mV and a frequency of 15 Hz.

UV–vis absorption spectra were obtained using classical 1 cm quartz cells by means of Perkin Elmer—Lambda 25 spectrophotometer. TEM images were taken with Libra 120, Zeiss. Scan electron microscopy (SEM) images were recorded using Merlin, Zeiss scanning electron microscopy equipped with EDS. The conditions used for SEM determination were set as follows: accelerating voltage, 10.0 kV; working distance, 6.1 mm; and coating Au.

2.2. Reagents

Tris-HCl, methylene blue, hexaammineruthenium(III) chloride (RuHexCl), concentrated HCl (36.5–38.0%), $ClCH_2COOH$, $NaNO_3$, NaOH, NaCl, KCl, 25% ammonium hydroxide, graphite powder, concentrated H_2SO_4 (95.0–98.0%), $K_2S_2O_8$, P_2O_5, $KMnO_4$ were purchased from Aldrich Chemicals, Germany. $K_3Fe(CN)_6$, $K_4Fe(CN)_6$ and $MgCl_2$ were purchased from Fluka Analytical, Germany. H_2SO_4, KCl, NH_3 and H_2O_2 were purchased from POCh, Poland. All reagents were of analytical grade and were used without further purification.

2.3. Solutions

The following solutions were prepared: 50 mmol L^{-1} Tris-HCl, 5 mmol L^{-1} $K_3Fe(CN)_6/K_4Fe(CN)_6$ in 100 mmol L^{-1} KCl, 10 μmol L^{-1} methylene blue in 50 mmol L^{-1} Tris-HCl. The voltammetric measurements were carried out in 50 mmol L^{-1} Tris-HCl, or 50 mmol L^{-1} Tris-HCl solutions containing appropriate concentrations of methylene blue or hexaammineruthenium(III). The EIS measurements were performed in 5 mmol L^{-1} $K_3Fe(CN)_6/K_4Fe(CN)_6$ in 100 mmol L^{-1} KCl. The pH was adjusted with 1 M NaOH or HCl water solution. All solutions were prepared with Milli-Q water.

2.4. Methods

2.4.1. Glassy carbon electrode cleaning

Before any electrochemical measurements, the glassy carbon electrode was polished with alumina powder of grain sizes from 1 to 0.05 μm (CH Instruments, USA). Then, the electrode was rinsed with demineralized water and sonicated for 2 min at 40 °C and again rinsed with demineralized water. The last step of electrode cleaning was its voltammetric cycling in 50 mol L^{-1} Tris-HCl solution (pH 5), until the CV characteristic for a clean glassy carbon was obtained.

2.4.2. GO synthesis

GO was synthesized from natural graphite powder by the method of Hummers and Offeman [24]. Prior to the GO preparation a preliminary graphite oxidation was done. The graphite powder (4 g) was put into an solution containing concentrated H_2SO_4 (6 mL), $K_2S_2O_8$ (2 g), P_2O_5 (2 g) heated up to 80 °C. The resultant dark blue dispersion was allowed to cool to room temperature. Then the solution was diluted with 5 L of distilled water, filtered, and washed on the filter until the rinse water pH became neutral. The product was dried in air at ambient temperature overnight. The resultant powder was subjected to oxidation by Hummers' method. The preliminary oxidized graphite powder (4 g) was put into cold (0 °C) concentrated H_2SO_4 (92 mL). Then the $KMnO_4$ (12 g) was gradually added with stirring and cooling, so that the temperature was not allowed to reach 20 °C. The dispersion was stirred at 35 °C for 2 h. After that the distilled water (185 mL) was added. After 15 min the reaction was terminated by the addition of a large amount of distilled water (0.6 L) and 30% H_2O_2 solution (10 mL). The color changed to bright yellow. Dispersion was filtered and washed with 1:10 (v/v) HCl solution (1 L) in order to remove metal ions. The GO product was suspended in distilled water to give a viscous, brown, 2% dispersion. Then it was subjected to dialysis to completely remove metal ions and acids.

2.4.3. Carboxylated GO synthesis (GCOOH)

Carboxylated graphene oxide was prepared according to Ref. [25]. GO prepared with the above mentioned procedure was subjected to 1 h sonication. The resultant suspension (50 mL) was mixed with NaOH (0.6 g) and $ClCH_2COOH$ (0.5 g). The mixture was bath sonicated for 2 h to convert the hydroxyl groups of the GO to —COOH moieties. The resulting GCOOH solution was neutralized