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CARBON NANOTUBES AS ELECTRODES OF ELECTROCHEMICAL SENSORS

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Electrochemical sensors have large perspectives for exploration to presence of toxic compounds in environment determination. It have been shown advantages of paste electrodes of multi-walled carbon nanotubes to mercury (II) and chromium (VI) content in aqueous medium determination. The role of oxygen-containing groups at the nanotubes tips to the metal ions adsorption was discussed. These electrodes allow to determinate Hg (II) content in water at the lowest limit of 20 ng$\cdot$dm^{-3} and Cr (VI) in concentration interval of 50–150 mcg$\cdot$dm^{-3}.

INTRODUCTION

Continuous monitoring of environment to presence of toxic compounds deals with a world problem. That leads to necessity of elaboration of new reliable, fast, and inexpensive methods for determination of toxic compounds content at super low concentrations. The chromatographic methods demand of the expensive equipment exploration and long duration. Therefore great attention is paid to elaboration of sensor and biosensor methods for toxic compounds determination.

One of the most perspective directions is exploration of the methods that base on investigation of electrochemical phenomena. A great advantage of electrochemical analysis is that response of the system is obtained as an electrical signal. That ensures high speed and accuracy of analysis and gives the possibility for automatic reductions of obtained results. A sensor sensitive to change of an analyte concentration can work on the base of measuring current magnitude at constant potential (amperometry) or its linear scan (voltammetry) and of the equilibrium potential of an indicator electrode for that the investigated substance is potential determinative. A response magnitude of sensor to change of an analyte concentration depends on both capability of an electrode surface to adsorb selectively analyte molecules and electrocatalytic activity of an electrode material in redox reactions of determined substance. Therefore, nowadays a considerable attention is paid to development of new generation of electrochemical sensors with chemical modified electrodes. For modification of an electrode surface, nanomaterials can be used. Due to structure and size dependence of their chemical and physical properties, electrodes modified with nanomaterials have peculiar electrochemical characteristics. Among the new classes of nanostructured materials, carbon nanotubes constitute a promising class of advanced nanomaterials with outstanding electronic, chemical, structural, optical, mechanical and thermal properties for practical application including nanodevices and nanosensors. Due to their peculiar hollow structure, nanosized morphology (diameter of 1–10 nm), high specific surface area (100–2000 m^2/g), high carrier mobility, excellent chemical stability, carbon nanotubes are ideal candidates for highly sensitive sensors. It was interesting to employ the electrodes of carbon nanotubes to determination of highly toxic compounds mercury (II) and chromium (VI) in water.

As a rule, mercury content in natural water is of 0.1–20 ng$\cdot$dm^{-3}. The most dangerous is methyl mercury that is accumulated with fish tissues presents [1]. This causes low level of limit permissible concentration of its compounds in water (50 ng$\cdot$dm^{-3}) and highest requirements to sensitivity of the methods for determination of mercury in water. For determination mercury content the spectrophotometry, atomic adsorption spectrometryfluorometry, XR fluorescence, potentiometry, and voltammetry methods are employed [2]. The stripping voltammetry method is employed most often [3]. Carbon electrodes modified with gold nanoparticles [3, 4] or organic thiocompounds, for instance 2-amino-6-purinethiol, 5-amino-1,3,4-thiazol-2-thiol [5], 1,4-benzenedimethylthiol [6]. Modification of carbon paste electrodes with 2-aminothiazol molecules are covalent attached to silica-gel surface allows to lower the limit of determination to mcg·dm^{-3} [7].

The modified with gold nanoparticles carbon paste electrodes were used for determination of chromium (VI) content in natural water [8].

Necessity to modification of carbon paste electrodes is caused by low specific area of graphite that limits its adsorption capability. Carbon nanotubes have graphite structure but their specific area is 2 time higher. Due this fact the paste electrodes of carbon nanotubes for determination of mercury (II) and chromium (VI) content in water were used in the present paper.

EXPERIMENTAL

Multi-walled carbon nanotubes (MWCNTs) were prepared by using chemical vapor deposition (CVD) of benzene in argon flow of 700°C using Ni nanoparticles as catalyst. The catalyst was prepared by electrodeposition of nickel on the surface of thermoexfoliated graphite particles (the detailed procedures were described in our previous papers [9, 10]). 200 mg of the catalyst powder in a stainless boat was put into a tube quartz reactor that heated up to 700°C in an electrical furnace. Argon was flowed with velocity of 100 ml·min^{-1} though a vessel with benzene and reactor during of 50 hours. The suspension was filtrated and than rinsed with deionized water until the pH of the suspension reached about 6, and dried at 80^{o} C. The as-grown MWCNTs [11] contained 20% mass. of the catalyst that was removed by treatment of the product with the solution of 3 M HNO_3 for 48 h. If CVD is used for carbon nanotubes preparation depending on a catalyst, a reactive mixture composition and process parameters carbon threads can be obtained which consist of aligned nanotubes with graphene shits parallel to axis or fibers with angle or perpendicular shits to a tread axis. A conclusion about graphene shits disposition can be drawn on the base of XR diffraction data [12]. As one can see in Fig. 1, prepared carbon material has graphite structure. Maximum at 52.7^{o} shows to presence of highly oriented pyrolytic graphite admixtures.

Cyclic voltammetry investigation were carried out in a conventional three electrode one compartment glass electrolytic cell using a PI-50-1.1 potentio-galvanostat connected via analog-to-digital converter with PC.

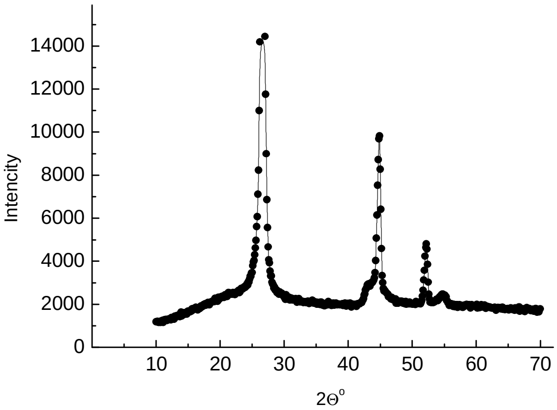


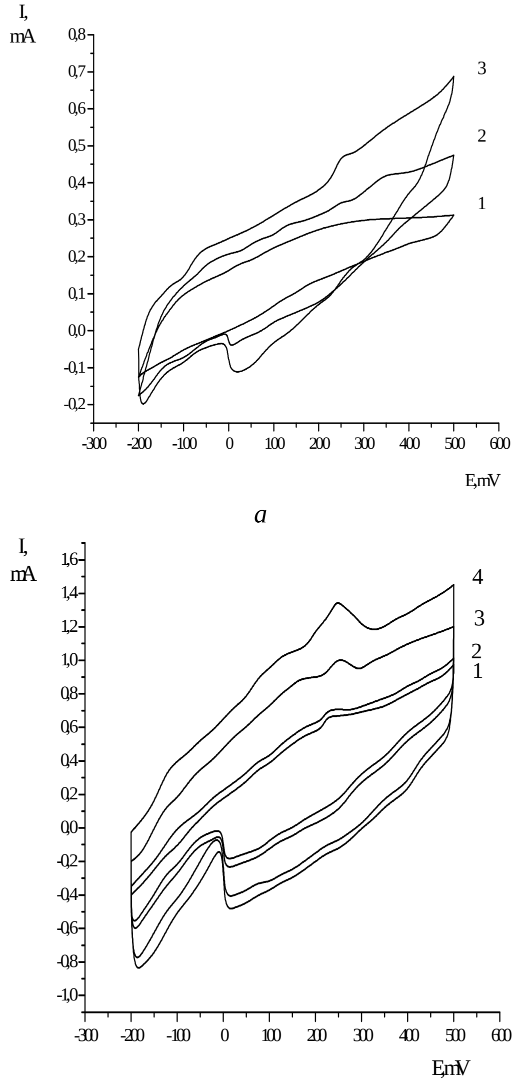
Fig. 1. XRD pattern of prepared carbon nanotubes

The auxiliary electrode was a glassy carbon rod with diameter of 2 mm. The reference electrode was a saturated Ag/AgCl electrode connected to the cell solution through the Luggin capillary. All potentials values mentioned in the text are given against Ag/AgCl electrode only. A paste for working electrodes was prepared by mixing MWCNTs powder with appropriate amount of liquid paraffin and through hand mixing in a mortar and pestle (~90:10, w/w, %). A portion of the composite was placed into the end of a glass tube (ca. 3 mm i.d.). Electrical contact was made by a copper pin down into the back of the composite. To produce a "fresh" working electrode surface, 1 mm of the paste was pushed out and cut off.

All chemicals were purchased of analytical grade and used in the experiments directly without any further purification. All solutions were prepared using deionized water.

RESULTS AND DISCUSSION

The volammetric methods for non-ferrous metals determination (if content is less than 1 mcg·dm^{-3}) base on anodic dissolution of a metal film deposited on a working electrode surface at a stage of preliminary electrolysis by cathode polarization it in an investigated solution. To an electrochemical reaction proceeding and deposition of a metal film, there is a necessity of adsorption interaction between electroactive particles and presence of electrode surface. Adsorption occurs on active centres only at solid surface. Adsorption sites of CNT are assumed to be the carboxyl groups formed at the nanotubes tips on treatment with nitric acid [13]. The presence of the hydroxyl groups was assumed too [14]. Since the side walls of the nanotubes are like basal sheets of graphite, slow electron transfer is characteristic of them and opened tips are like edges of graphite sheets, the oxygen-containing functional groups are formed at the CNT tips. These are polar groups with a negative charge capable to stable complexes with metal cations due to ion exchange. Due to this all metal is deposited on an electrode surface at the stage of preliminary electrolysis since its duration is 5–10 times higher than it is needed to all mercury being in a solution extraction. The voltammograms obtained at polarization of the electrode of carbon nanotubes in the solutions with different mercury content are shown in Fig. 2.



b

Fig. 2. Voltammograms of CNT electrode in solutions with different content of mercury; (*a*): *1* – supporting electrolyte; *2* – 0.02; *3* – 0.04 mcg·dm^{-3}; (*b*): *1* –0.1; *2* – 0.5; *3* – 1; *4* – 2 mcg·dm^{-3}

The value of limit current displays a linear dependence of both the mercury concentration and of the potential scan rate that shows to diffusion control of reaction rate.

Since oxygen reduction reaction proceeds at the potentials lower -0.2 V at the carbon nanotubes electrodes, voltammograms were recorded in the potential interval of -0.2 to +0.5 V. An electrolyte agitation was carried out by Argon bubbling. After current on the working electrode was cathode polarized at linear potential sweep with scan rate of 1 mV·s^{-1}. When potential of -0.2 V was achieved electrolysis in duration of 200 s was carried out. At the stage of preliminary investigations it was found that duration of electrolysis in the interval of 50–500 s does not influence to limit current value. At long time of accumulation for voltammograms of gold modified electrodes two peaks can be displayed that are charged with mercury dissolution of the electrode surface and mercury dissolved in gold [4]. That gives advantages to the carbon nanotubes electrodes over the modified with gold electrodes as necessity to optimal time for accumulation determination. After deposition of mercury on the working electrode surface it was polarized to anode direction at scan rate of 10 mV·s^{-1}. At higher scan rates limit current plateaus don't display enough clear at voltammograms especially in the electrolytes with mercury concentration lower than 1 mcg·dm^{-1}.

In contrast to the modified with gold electrodes, on that mercury dissolution proceeds in potential interval of +0.5 to +0.6 V [3] limit currents displays on voltammograms of carbon nanotubes electrodes at the potential of +0.25 V as of modified with organic compounds. That allows to avoid the iron (III) influence that reduced to iron (II) in electrolysis process. At the stage of anode swap Fe (II) is electrooxidized to Fe (III) in the potential interval of +0.4 to +0.6 V that complicates the mercury dissolution current measurements. The carbon nanotubes electrodes allows to determinate of mercury content in water by the inversion voltammetry method at the lowest concentration of 20 ng·dm^{-3}.

Among the heavy metal pollutants, chromium is considered as a high priority environmental pollutant. Chromium exits in environment mainly in two states: trivalent Cr (III) and hexavalent Cr (VI). Cr (III) is an essential element in humans and is much less toxic than Cr (VI). Due to the severe toxicity of Cr (VI), the EU Directive, WHO and US EPA have set the maximum contaminant concentration of Cr (VI) in domestic water supplies as 0.05 mg·dm^{-3}. Chromium (VI) is primarily present in the form of chromate (CrO_4^{2-}). As it have been shown above the functional groups at the ends of carbon nanotubes form negative charge on the electrode surface that leads to repulse of anions [15] and essential decrease in CrO_4^{2-} ions adsorption. For shielding of negative charge the polyaniline film has been deposited on the electrode surface by cycling of the electrode in 10^{-3} mol/l aniline solution in 1M H_2SO_4 20 times in the potential interval of 0 to +0.8 V at scan rate of 20 mV·s^{-1}. Nitrogen atoms have positive charge in polyaniline film that gives to the electrode surface capability for hydrogen bonds with oxygen-containing groups of organic compounds or anions. Due to that adsorption capability of the working electrode surface with respect to CrO_4^{2-} – anions essentially increase and the sensitivity of voltammetric method for chromium containing in water determination rises. If limited current plateaus are displayed at voltammograms of unmodified carbon nanotubes electrodes when chromium concentration is higher than 1 mg·dm^{-3} the modified electrodes allows to determinate of Cr (VI) concentration in the microgram interval (Fig. 3).

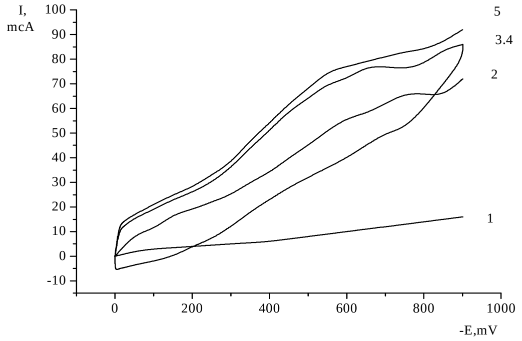


Fig. 3. Voltammograms of the electrode of carbon nanotubes modified with polyaniline film in the chromium containing solutions: *1* – 0, *2* – 50; *3* – 100; *5* – 150 mcg·dm^{-3}; *4* – anodic branch of the curve 3, scan rate 1 mV·s^{-1}

It is particularity of the polyaniline films absence of electrochemical activity and conductivity in the solutions at pH > 4. Due to that the voltammetric curve of modified electrode doesn't distinguish that of the unmodified electrode one in the supporting electrolyte solution. Any red-ox transformations don't proceed at the electrode if depolarizator is absent. For the voltammograms obtained in the electrolytes containing dichromate potassium the presence is character the limited current plateaus. Their magnitudes are depended both on chromium concentration and on scan rate. A linearity of the limited current magnitude versus chromium content in the solution occurs up to concentration of 150 mcg·dm^{-3}.

CONCLUSION

It has been shown the effectiveness of the carbon nanotubes working electrodes for use in the voltammetric sensors for mercury (II) and chromium (VI) content in water determination. It is necessary to modify the electrode surface with polyaniline film for chromium (VI) determination.

REFERENCES

1. *Hammershmidt C.R., Fitzgerald W.M.* Methylmercury in fresh water, fish linked to atmospheric mercury deposition // Environ. Sci. Technol. – 2006. – V. 40, N 24. – P. 7764–7770.
2. *Hassan S.S.M., Saleh M.B., AbdelGaber A.A. et al.* Novel mercury (II) ion-selective polymeric membrane sensor based on ethyl-2-benzoyl 2 phenylcarbamoil acetate // Talanta. – 2000. – V. 52, N 2. – P. 285–293.
3. *Tsapko Yu.V., Ermakov S.S., Moskvin L.N.* A rapid version of standardless stripping voltammetry for determining mercury in aqueous solutions // J. Anal. Chem. – 2008. – V. 63, N 10. – P. 971–974.
4. *Khustenko L.A., Larina L.N., Nazarov B.F.* Rapid determination of mercury in water by stripping voltammetry at a gold modified carbon electrode // J. Anal. Chem. – 2003. – V. 58, N 3. – P. 262–267.
5. *Cupta V.K., Singh A.K., Al Khayat M., Gupta B.* Neutral carriers based polymeric membrane electrodes for selective determinations of mercury (II) // Anal. Chim. Acta. – 2007. – V. 590, N 1. – P. 81–90.
6. *Riskin M., Basnar B., Katz E., Willner I.* Cyclic control of the surface properties of a monolayer-functionalized electrode by the electrochemical generation of Hg monoclusters // Chem. Eur. J. – 2006. – V. 12, N 33. – P. 8549–8557.
7. *Filho N.L., Carmo D.R., Rosa A.H.* An electroanalytical application of 2-aminothriazole-modified silica gel after adsorption and separation of Hg (II) from heavy metals in aque-

ous solution // Electrochim. Acta. – 2006. – V. 52, N 3. – P. 965–972.

8. *Gevorgyan A.M., Vakhnenko S.V., Artykov A.T.* Determinatin of chromium in water by stripping voltammetry // J. Anal. Chem. – 2004. – V. 59, N 4. – P. 371–373.
9. *Zagorowsky G.M., Prikhodko G.P., Ogenko V.M., Sydorenko I.G.* Extraction of copper from diluted solutions at dispersed graphite electrodee // J. Appl. Chem. – 2001. – V. 74, N 3. – P. 476–478 (in Russian).
10. *Ogenko V.M., Sydorenko I.G., Prikhodko G.P., Zagorowsky G.M.* Electrodeposition of nickel at graphite three-dimensional electrode // Ukr. Chem. J. – 2002. – V. 68, N 9. – P. 36–39.
11. *Zagorowsky G.M. Sydorenko I.G., Chuiko A.A.* Preparation of carbon nanostructures by benzene pyrolyzis over thermoexfoliated graphite with electrodeposited nickel // Nanosystems, Nanomaterials, Nanotechnologies. – 2004. – V. 1, N 1. – P. 165–171.
12. *Park C., Engel E.S., Growe A. et al.* Use of carbon nanofibers in the removal of organic solvents from water // Langmuir. – 2000. – V. 16, N 21. – P. 8050–8056.
13. *Chen J., Hamon M.A, Hu H. et al.* Solution properties of single-walled carbon nanotubes // Science. – 1998. – V. 282, N 5386. – P. 95–98.
14. *Hu J., Chen C., Zhu X., Wang X.* Removal of chromium from aqueous by using oxidized multiwalled carbon nanotubes // J. Hasard. Mater. – 2009 – V. 162. – P. 1542–1550.
15. *Silva C.P., Carapuca H.M.* Glassy carbon electrodes coated with poly(allylamine hydrochloride), PAH: Characterization studies and application to ion-exchange voltammetry of trace lead (II) at combined PAH/mercury film electrodes // Electrochim. Acta. – 2006. – V. 52. – P. 1182–1190.

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Електроди з вуглецевих нанотрубок в електрохімічних сенсорах

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Електрохімічні сенсори мають значні перспективи для використання як аналізаторів для визначення наявності в оточуючому середовищі токсичних сполук. Показані переваги пастових електродів із багатостінних вуглецевих нанотрубок для визначення вмісту ртуті (II) і хрому (VI) у водному середовищі. Розглядається роль кисневмісних функціональних груп в процесі адсорбції іонів металів. Такі електроди дозволяють визначати вміст Hg (II) у воді при її мінімальній концентрації 20 нг·дм$^{-3}$ *і Cr (VI) в інтервалі концентрацій 50–150 мкг·дм*$^{-3}$.

Электроды из углеродных нанотрубок в электрохимических сенсорах

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Электрохимические сенсоры имеют большие перспективы для использования в качестве анализаторов для определения наличия в окружающей среде токсичных соединений. Показаны преимущества пастовых электродов из многостенных углеродных нанотрубок для определения содержания ртути (II) и хрома (VI) в водной среде. Рассматривается роль кислородсодержащих функциональных групп в процессе адсорбции ионов металлов. Такие электроды позволяют определять содержание Hg (II) в воде при ее минимальном содержании 20 нг·дм$^{-3}$ *и Cr (VI) в интервале концентраций 50–150 мкг·дм*$^{-3}$.